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CELLULOSE ESTER VARNISHES

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OIL & COLOUR CHEMISTRY MONOGRAPHS
Edited by R. S. Morrell, M.A., Ph.D., F.I.C.

CELLULOSE ESTER VARNISHES

BY

F. SPROXTON, B.Sc., F.I.C.
(British Xylonite Company, Ltd.)

FRANKLIN INSTITUTE
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CONS.
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S77
1925a

NEW YORK
D. VAN NOSTRAND COMPANY
EIGHT WARREN STREET
1925

PRINTED IN GREAT BRITAIN

Nov 1925
Publ
4.50

Richard Clay & Sons, Ltd., Printers, Bungay, Suffolk.

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AUTHOR'S PREFACE

The primary purpose of a preface is to disarm the critic, but the author of a book is usually so keenly aware of its shortcomings that only the major criticisms can be anticipated before it passes into the hands of readers. Worden's immense volumes contain such a complete account of the facts known about the derivatives of cellulose, that an author writing on the same subject, or any part of it, must be to some degree a plagiarist. There seems to be room, however, for a small book on the cellulose ester varnishes which, while not dealing exhaustively with any part of the subject, may nevertheless be individual enough in outlook to be something more than a guide to the larger reference books. I have thought it possible that such a book might be useful to the manufacturer of the varnishes, particularly to chemists entering the laboratories of such manufacturers; to the user of the varnishes, who may be interested to know more of the nature of, and the problems associated with, the materials with which he works; and, lastly, to the student, who may obtain a bird's-eye view of a growing industry based on the principles of colloid chemistry, and who may, perhaps, find some suggestions for research.

Many references will be found to the excellent specifications for aircraft materials issued by the British Engineering Standards Association, which should be in the hands of all manufacturers of these varnishes. A few minor criticisms of detail will be found in the text of the book. The only general criticism I wish to make is that where the information in the specifications is derived from chemical literature, the principal references might be quoted. This practice would frequently assist the chemist who applies the specifications to materials in the laboratory; it would also ease the conscience of an author anxious not to infringe copyright.

Patent literature has been scantily used, and then only *faute de mieux*. A perusal of the patent literature of the cellulose esters generates more heat than light, and it is frequently difficult to separate the wheat from the chaff. Wherever possible, the attention of the reader has been drawn to processes which have actually been employed on a large scale. It will be evident from the list of references that no single journal ministers to the entire needs of the industry. The excellent abstracts of the Journal of the Society of Chemical Industry, *Chemistry and Industry*, will keep the reader in touch with all new developments, but the original papers must often be consulted. Another useful English publication is the *Journal* of the Oil and Colour Chemists' Association. Industrial developments can be followed in *Kunststoffe*, and scientific developments

in colloid chemistry in the *Kolloid Zeitschrift*. Useful information often appears in *Le Caoutchouc et La Gutta Percha*, but is sometimes not original.

Nomenclature is a difficult problem in a scientific book written on a technical subject. The word "nitro-cellulose," for example, is scientifically incorrect; yet it is firmly established in the industry and it is accepted by the learned Society which at one time used to alter the substantive "smell" to "odour," and presumably thought the patriarch's description of Esau indelicate. "Nitro-cotton" is scientifically worse, but actually less objectionable (if applied to nitrated cotton cellulose) since it makes no pretence of scientific derivation. On the whole, the best plan seems to be to use the terms "cellulose acetate" and "cellulose nitrate" where scientific comparison or contrast is drawn, and elsewhere to use the customary names indiscriminately. Similar considerations apply to some of the solvents.

My thanks are due to the directors of the British Xylonite Company, Ltd., for permission to write this book; to my colleague, Mr. A. M. Hutchison, B.Sc., who has read the manuscript and made many valuable suggestions; and to the following bodies for permission to reproduce, in some instances with slight modifications, drawings which have appeared in their publications :—

The Council of the Chemical Society for Figs. 3 and 4.
The Council of the Society of Chemical Industry for Fig. 2.
The Council of the Faraday Society for Fig. 8.
The Aeronautical Research Committee for Figs. 5 and 6.
The Council of the Franklin Institute for Fig. 7.

F. S.

Brantham Works,
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CELLULOSE ESTER VARNISHES

CHAPTER I

INTRODUCTION

Cellulose Nitrate and Acetate—Solubility in Volatile Solvents—Polymerised Structure—Nomenclature of the Solutions—History of Cellulose Nitrate—Schönbein, Hadow, Scott Archer, Alexander Parkes—Stevens and Amyl Acetate—Search for Technical Solvents—Commercial Developments—Economic Considerations—History of Cellulose Acetate—Schützenberger to Cross and Bevan—Miles's Process of Partial Hydration—War Expansion—Aeroplane Dopes—Shortage of Solvents—Post-war Developments.

CELLULOSE is familiar to everyone in various forms, such as cotton wool, cotton thread, calico, and linen. The paper on which most newspapers are printed contains wood pulp, an impure form of cellulose. Cellulose itself is not easily dissolved, and its solutions are not suitable for use as varnishes. Under certain conditions, however, it may be made to combine with acids, and the compounds formed are termed " cellulose esters."

Only two esters of cellulose are of any importance in the varnish industry, namely, the nitrate and the acetate, formed by the combination of cellulose with nitric acid and acetic acid respectively. These substances are soluble in certain mixtures of organic liquids which have a comparatively high rate of evaporation, and when the solutions are spread on solid surfaces they rapidly become dry, leaving the cellulose ester in the form of a continuous film. By making certain additions to the original solutions, the hardness and adhesiveness of the films may be modified. Owing to the rapidity with which the solutions dry, they may be applied at ordinary temperatures, although a warm room is advantageous. As a rule a coating is dry in a few hours.

All organic protective coatings consist of highly polymerised structures. The chief distinction between the cellulose ester varnishes and the oil varnishes is that, in the former, this polymerised structure already exists, whereas the polymerisation of oil varnishes takes place to a large extent after application. The degree to which the original cellulose is de-polymerised or degraded in structure before and during the manufacture of the ester determines to a considerable extent the properties of the resulting varnish.

Properties of Cellulose Ester Varnishes.

The cellulose ester varnishes occur in commerce as more or less viscous solutions, which may be either transparent or opaque. The transparent varnishes may be coloured in practically any tint,

so as to give a coloured transparent coating. These are usually termed lacquers. The opaque varnishes may also be obtained in any colour and are usually termed enamels. As a rule they are made so as to dry with a bright surface, but the enamels are sometimes required to dry with a dull or matt surface. It is becoming customary to include all solutions of cellulose esters used for protective or decorative coatings under the general term of " cellulose varnishes." The name is not a happy one, as the materials do not resemble the oil varnishes very closely, and they are not solutions of cellulose. To those accustomed to scientific terminology, " cellulose ester varnish " and " cellulose ester solution " would bear somewhat similar meanings, but " cellulose solution " would denote something very different. However, it is difficult to dislodge a trade name, which in this instance probably dates back to the discovery of " cellulose " by the public in 1916.

As all these varnishes are made with volatile organic solvents, they have characteristic smells which disappear when the coating dries. They may be applied by brush, but better results are obtained by dipping or by use of an air-spray. Under proper conditions, the solutions dry with a high polish, and the films resist water, petrol, soap, turpentine, weak acids and weak alkalies.

Cellulose Nitrate Solutions—Historical.

Although cellulose has been known from time immemorial, the history of cellulose nitrate solutions scarcely begins until the latter half of the nineteenth century. Pelouze,[1] in 1838, investigated the action of nitric acid on paper, linen, and cotton wool, but the importance of the products was first recognised by Schönbein,[2] who in 1845—6 prepared nitrates of cotton cellulose by a process which he kept secret. Otto [3] discovered and published the method of production a little later, and Knop [4] is said to have been the first to make use of a mixture of sulphuric and nitric acids, thereby laying the foundation of the modern cellulose nitrate industry. The papers in which these early discoveries are described are available in an English translation by MacDonald.[5] Schönbein and his collaborator Böttger, although they observed the solubility of their product in various organic liquids such as ethyl acetate, were chiefly interested in it as a substitute for gunpowder. An interesting review of the current state of knowledge of cellulose nitrate is given in Gmelin's " Handbook of Chemistry " (1872 edition),[6] although no notice is taken of such technical developments as those

of Parkes (*v. infra*). It was known by then that the properties of the product varied largely according to the composition of the acid mixture, the time and the temperature of nitration. Directions are given for the preparation of (*a*) an explosive pyroxylin, (*b*) a collodion-wool soluble in ether–alcohol, and for the preliminary treatment of the cotton with boiling soda solution and bleach. Various analyses of the product, by Schönbein, Crum, Pelouze, Gladstone and others, are given, showing percentages of nitrogen ranging from 9·3 to 14·26, while among the solvents quoted are ether–alcohol, ether alone, alcohol, ethyl acetate, glacial acetic acid, acetone, and wood spirit. The first important researches on the solubility of cellulose nitrate were carried out by Domonte and Ménard [7] (1846), who investigated the difference between ether-soluble and ether-insoluble products. Hartig [8] in 1847 stated that cellulose nitrate formed dark brown solutions with common camphor, oils, waxes and resins. This appears to be the first occasion on which cellulose nitrate and camphor were brought together, but his observations apply to heated mixtures and not to any product resembling either a modern celluloid varnish or solid celluloid.

The researches of Hadow [9] in 1855 on the relation between the composition of the acid mixture and the properties of the cellulose nitrate produced are of interest as the first of a long series of similar experiments by various chemists. The value of the observations recorded is in many cases discounted by the fact that the cellulose which formed the starting point is not rigidly defined. This aspect of the nitration of cellulose will be briefly developed later in the book.

The first attempts to find practical applications for solutions of cellulose nitrate were made in 1848 by Maynard [10] and Bigelow,[11] who suggested independently the use of a solution of cellulose nitrate in ether–alcohol (collodion) as a protective dressing for wounds. F. Scott Archer [12] in 1851 was the first successfully to use collodion in photography, and there is an interesting description of the preparation and use of collodion for this purpose in Robert Hunt's "Manual of Photography" (Griffin, 1853).* All of the early workers were confronted with the difficulty that these solutions contracted considerably on drying, causing puckering and unevenness, while at times the films would be more or less white and opaque instead of transparent.

Alexander Parkes, the greatest of the pioneers in the development of the industrial uses of cellulose nitrate, began work on the

* The writer is indebted to Mr. A. M. Hutchison for the loan of this book

subject in the early 'fifties. Although concerning himself chiefly with the manufacture of plastic solids, he investigated many liquid solvents and foresaw the value of the material as a base for varnishes. He recognised that the opacity frequently manifested by films from ether–alcohol solutions was due to precipitation of amorphous cellulose nitrate by absorption of atmospheric moisture, and was the first to employ anhydrous solvents. An early patent of his describes the dehydration of wood spirit (crude methyl alcohol) by distillation with calcium chloride.[13] This patent makes special reference to the use of solutions as protective coverings, and foreshadows many later developments, thus: "For a transparent and colourless substance I use a solution of guncotton alone or with gums or resins that will set transparent with it and this is applicable as a coating to silk tinsel articles or other textile fabrics, sewing cotton thread, worsted, string, felted goods, leather, plaster or wood." In the same specification Parkes also suggests the use of metallic bronzes with cellulose nitrate solutions. He recommends using thick solutions and spreading machinery, thereby producing films which can be used for bookbinding or button manufacture. Lastly, in order to render the film non-inflammable he recommends the incorporation of ammonium phosphate, magnesium phosphate, cadmium iodide, mercuric iodide, calcium oxalate, talc or alum.

Parkes realised that satisfactory films would not be obtained under ordinary atmospheric conditions from solutions of cellulose nitrate in solvents of low boiling point, and he investigated aniline and nitrobenzene. These, however, failed for the opposite reason, their vapour pressure being so low at ordinary temperatures that solutions would not dry in a reasonable time. The poisonous nature of the vapours was also a drawback. Acetic acid was obviously unsuitable on account of its unpleasant and corrosive vapour.

In 1864 Parkes [14] disclosed the strong solvent power possessed by solutions of camphor in oil of turpentine or in wood spirit. He was therefore the first to use camphor in useful conjunction with cellulose nitrate, and in a lecture given before the Royal Society of Arts in 1865 he describes the use of camphor as an important improvement in the manufacture of solid masses from pyroxylin, since it renders them more uniform and less contractile.

Pellen's patent of 1856 [15] for the use of collodion for covering toys and balloons is of interest in view of the immense development of aircraft dopes sixty years later.

The most interesting of Spill's [16] patents in reference to solvents

of cellulose nitrate is that in which he makes known the solvent power of a mixture of ethyl alcohol and benzene, each constituent being a non-solvent when employed alone. The study of these mixed solvents is one of the most interesting problems in the chemistry of cellulose nitrate. A mixture of ether and alcohol is one of the commonest solvents of cellulose nitrate, containing from 11·0 to 12·4% nitrogen, although neither constituent alone is a solvent at ordinary temperatures. It was employed by nearly all the early experimenters and was investigated by Saillard in 1859.[17] A careful but inconclusive research was carried out by Baker [18] in 1912, while as recently as 1921 Bancroft [19] has described it as one of the present problems of colloid chemistry.

Amyl Acetate.

Until the year 1882, the development of a large industry in solutions of cellulose nitrate was prevented by the fact that there were no cheap and otherwise desirable solvents and solvent mixtures known intermediate in boiling point between the group of low-boiling liquids such as methyl alcohol, acetone, ethyl acetate, ethyl alcohol, ethyl ether and benzene, and the high-boiling slow-drying solvents such as aniline and nitrobenzene. The gap was filled in 1882 by the discovery of the solvent power of amyl acetate by Stevens.[20] Crude amyl alcohol, the so-called fusel oil, is a by-product in the production of ethyl alcohol by fermentation, and for many years was of so little value that it was burned in lamps in the distilleries in place of paraffin oil. Stevens found that the acetate of amyl alcohol (strictly speaking, of the mixture of various amyl and other alcohols which fusel oil contains) possessed the blend of properties required for his purpose, namely, high solvent power for a large range of cellulose nitrates, a vapour pressure at ordinary temperatures low enough to prevent unduly rapid evaporation but high enough not to prolong the drying of the film, and very small affinity for water.

Search for Technical Solvents.

The search for solvents of cellulose nitrate has continued right down to the present day, but since the discovery of the solvent power of amyl acetate there have not been very many additions to the list which have had much influence on the varnish industry. The acetins (acetates of glycerol) were patented by Schüpphaus in 1889.[21] F. Crane [22] patented the use of acetone oil (a mixture of indefinite

composition remaining from the fractionation of acetone) in 1892, and a large number of compounds, including some esters which have had a limited application in the varnish industry, were patented by A. Nobel, from 1889 onwards.

The earliest commercial development of cellulose nitrate varnishes took place in the United States. The Stevens patents belonged to the Celluloid Company of New Jersey, while Hale and Crane formed the Crane Chemical Company and began the manufacture of varnishes and lacquers in 1886. The usefulness of the lacquers is greatly increased by the incorporation of resins, such as shellac, mastic and copal. Experiments in this direction date back at least to the 1855 patent of Parkes already quoted, but the first products of the type of modern lacquers, in which cellulose nitrate is blended with a resin in a mixture of solvents of graded volatility, were due to Field.[23] Such varnishes are more adhesive than those prepared with cellulose nitrate alone, and can be made with a higher solid content for the same degree of fluidity. At the present time they form a large proportion of the total output.

Economic Considerations.

In deciding the suitability of any substance as an industrial solvent for cellulose nitrate, economic considerations must come first. So much is known about the chemical groupings which impart solvent power to an organic molecule that it is safe to say an expert organic chemist could, if it were worth while, make extensive additions to the list of cellulose nitrate solvents; but only those substances which can compete in price with the known solvents have any chance of industrial application. Occasionally the development of chemical industry may result in a group of solvents, hitherto of academic interest only, becoming industrially available. For example, the fermentation of starch to butyl alcohol and acetone was originally developed to yield butyl alcohol for the manufacture of artificial rubber.[24] The acetone was absorbed in the explosives and varnish industries. During the Great War, acetone became the more important product, and as artificial rubber became of negligible account in England, butyl alcohol and butyl acetate became available as substitutes for amyl alcohol and amyl acetate. Since amyl acetate tends to become increasingly scarce, owing to the demands of the film and varnish industry and the diminution of spirit manufacture in the United States, butyl acetate has become a normal solvent in the cellulose ester industry.

Unless, however, the discoverer of a new solvent for cellulose esters sees some probability of the material being available at a price not greater than that of the usual solvents, it is not worth while for him to seek patent protection.

Cellulose Acetate—Historical.

Shortly after the time when Parkes began working on the industrial possibilities of cellulose nitrate, another industrial ester of cellulose, the acetate, was first prepared by Schützenberger.[25] The principal difference between the nitration and the acetylation of cellulose is that whereas cellulose nitrate is insoluble in the "spent acid," *i.e.*, the weakened mixture of sulphuric and nitric acid remaining after nitration of the cellulose, cellulose acetate is soluble in acetic acid. Hence, unless special indifferent diluents are added to the acetylation mixture, the cellulose passes into solution as acetylation proceeds, yielding a viscous mixture from which cellulose acetate is precipitated by the addition of water. In Schützenberger's first paper, he described the preparation by heating cellulose with acetic anhydride in sealed tubes to 130—140° C. In a later publication he recommended a temperature of 180° C., obtaining a product insoluble in alcohol or ether, and easily saponified by caustic alkalies.

The use of acetic anhydride under pressure was avoided by Franchimont's discovery of the so-called catalytic action of sulphuric acid or zinc chloride.[26] This step really marks the foundation of the modern cellulose acetate industry. Cross and Bevan used the zinc chloride method in their investigations of the constitution of the ligno-celluloses.[27] These investigators took out a patent in 1894 [28] for a method of acetylation involving the use of zinc chloride. The product was soluble in chloroform, yielding films which were suggested as substitutes for collodion in surgery. It is with this patent that the industrial history of cellulose acetate may be said to begin.

The technical development of cellulose acetate was much hindered by the slowness of the reaction between cellulose and the acetylating agents, and the limited range of solubility of the acetates produced. Investigators were therefore led to experiment on the acetylation of modified forms of cellulose, *i.e.*, cellulose which has been rendered more open to attack by partial degradation of its structure. Girard [29] had applied the name of hydrocellulose to the derivatives obtained by the mild acid hydrolysis of cellulose, and Lederer [30] found that

hydrocellulose could be acetylated more smoothly and at a lower temperature than unmodified cellulose. F. Bayer & Co.[31] patented a similar process almost at the same time.

So far the cellulose acetates produced had not been soluble in any of the useful organic solvents unless hydrolysis had been carried so far that the films left on evaporation were so brittle as to be technically useless. A great advance was made by Miles,[32] who found that by a partial hydrolysis of the primary product of acetylation, an acetate soluble in acetone was produced. In 1906 the Bayer Co.[33] patented an adaptation of Miles's process, and in 1907 they placed on the market varieties of cellulose acetate described as Cellite L and Sericose. These produced moderately good films when evaporated on glass, and were intended as textile finishes. The solvents employed for Cellite L were acetone or a mixture of ethyl acetate and alcohol. Sericose was insoluble in anhydrous acetone, but soluble in aqueous acetone or in acetic acid, either concentrated or somewhat dilute. It is evident that these substances were acetyl derivatives of a highly depolymerised cellulose. The acetic acid was not firmly held, as both the solid materials and their solutions rapidly developed a smell of free acetic acid. Owing to their high price (about seven shillings per pound) they never came into common use.

Eichengrün discovered the solubility of certain varieties of cellulose acetate in a hot mixture of benzene and alcohol and did much to develop the acetate varnishes. The later history of the acetate and its manufacture on a commercial scale by the Usines du Rhône, Dreyfus, and F. Bayer & Co., will be briefly sketched in a later chapter.

War Expansion.

An enormous development in the use of cellulose ester varnishes was brought about by the Great War of 1914—18, particularly in regard to cellulose acetate solutions. It had been found previous to the war[34] that these solutions, when applied to textile fabrics stretched on a frame, possessed the valuable property of shrinking and drawing the fabric taut. This property was utilised for making taut the wings of aeroplanes and protecting the fabric from the weather. It was subsequently found that by adding appropriate ingredients to the solutions the destructive effect of bright sunlight on the fabric could be considerably diminished. Similar effects can be produced with solutions of cellulose nitrate, but since the total thickness of the coatings applied to the fabric is quite considerable,

and the fabric itself is combustible, the use of cellulose nitrate alone adds appreciably to the fire danger, especially when the machines are used on active service.

Cellulose acetate was not manufactured in this country before the war, and the needs of the Government after the outbreak of war were met for a time by the importation of the material, chiefly from Switzerland and France. This arrangement, however, had finally to come to an end, owing to the great expansion in the demand, and a factory for the manufacture of cellulose acetate base and varnishes was established with Government assistance near Derby. Since the conclusion of the war, the demand for cellulose acetate dopes has naturally diminished, and the manufacturers have given their chief attention in this country to the production of artificial silk (rayon) from cellulose acetate.

This, however, was by no means the end of the difficulties. The principal solvent for cellulose acetate was acetone, a product of the distillation of wood, and during the early part of the war acetone was needed, not only for cellulose acetate varnishes, but also for the still more important material cordite. Certain wood distillation factories were established in this country, and the fermentation process by which acetone (and butyl alcohol) are produced from starch was developed. Nevertheless, the bulk of the country's requirements in acetone was imported, and since the demand exceeded the supply, and there were many other claims on the available shipping capacity, it became imperative to restrict the use of acetone as much as possible. Hence a great deal of research was carried out in two or three years which would probably have been spread over many years in times of peace. These researches had for their object to find the most economical way of using imported solvents, and involved numerous investigations into the changes of solvent power caused by mixing different liquids together, and into the resulting variations in viscosity of solutions of cellulose acetate made up from the mixtures.

In the explosives industry, the shortage of acetone required for cordite was still more severely felt, and led in time to the radical alteration of service cordite.[35] Instead of guncotton, which is a nitrate of cellulose containing about 13·0% of nitrogen, soluble in acetone but insoluble in any other available low-boiling solvent, the new cordite (R.D.B.) was made from a collodion cotton, containing about 12·4% of nitrogen, soluble in a mixture of ether and alcohol, and resembling a varnish nitro-cotton. Since ether is made from alcohol, and alcohol is cheaply and easily made from

molasses or any material containing starch, the use of acetone or any other product of the distillation of wood in the manufacture of cordite was thus entirely avoided. This change of solvent, however, involved, not only investigations into the best proportions of ether and alcohol to be used as the solvent, but also fundamental work on cotton cellulose itself, since it was found that cotton from different sources might give nitrates so different in solubility that not only the consumption of solvent but also the output of the new cordite were gravely affected.

The war also caused a considerable expansion in the use of solutions of cellulose nitrate for cementing the joints of celluloid accumulator cases, and for fixing glass to celluloid in the eyepieces of gas masks.

Since the war, some of the information gained in the Government factories has been published, and is influencing the development of industry. The most interesting advance is in the use of cellulose nitrate solutions of much greater fluidity than formerly. It must be understood that the high viscosity of these solutions imposes a practical limit on the amount of cellulose nitrate that can be dissolved in the solvents, since it is obvious that they must be fluid enough to flow somewhat like a paint. By preparing cellulose nitrate which yields solutions of greatly increased fluidity, it is possible to dissolve more of the ester than before without exceeding this practical limit, and a varnish is thus obtained which yields a much thicker coating for the same expenditure of labour and solvent. These very fluid cellulose nitrate varnishes have been developed chiefly in the United States, but the process of manufacture has been kept secret.[36]

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CHAPTER II

CELLULOSE

Cellulose—Elementary Formula—Cotton Cellulose—Sources—Chemical Reactions—Chemical Constitution—Formula of Irvine and Hirst—Views of other Investigators of Cellulose—*X*-Ray Evidence—Viscosity of Cellulose and its Esters in Solution—Significance of High Viscosity.

In this volume it is only necessary to discuss cellulose in relation to its esters and the solutions made from them. Cellulose may be described as the chief constituent of the skeleton of all vegetable bodies. Elementary analysis shows it to belong to the group of organic bodies known as the carbohydrates, and to have the composition $C_6H_{10}O_5$. Its physical and colloidal characteristics indicate that we must regard it as a polymer of the simple formula, and it is usually written as $(C_6H_{10}O_5)_n$. The latest researches on its constitution show that there may be two varieties of polymerisation in the cellulose structure, so that we might write it as $[(C_6H_{10}O_5)_n]_m$, n being probably a small integer and m a large and probably variable number.

The kind of cellulose used commercially for the manufacture of esters is almost entirely cotton cellulose, although wood cellulose has been used, particularly for the manufacture of cellulose nitrate, when supplies of cotton have been short [1, 2, 3]. Cotton is the purest form of cellulose produced by nature in large quantities, and contains about 90% of cellulose. The coniferous woods which form the source of wood cellulose contain about 60%,[4] and therefore require a greater degree of purification to isolate the cellulose.

Cotton is cultivated industrially chiefly in the United States and in India. The cotton fibres or hairs are attached to seeds contained in the " boll " or seed-pod of the cotton plant. When the bolls ripen they burst open, and the white mass of cotton fibre, after being freed from the seeds, forms the raw material of the spinning industry.

The chemical reactions which the constitutional formula of cellulose must explain are conveniently summarised by Green [5] and are quoted by Hall.[6] It is not necessary to give the complete list here, but the following properties have a bearing on the specification of cotton and its use in the cellulose ester industry :—

(*a*) The highest stage of nitration or acetylation is a triester calculated on a C_6 formula.

(*b*) Cellulose does not contain free carbonyl (aldehydic or ketonic) groups, but such groups are formed by simple hydrolysis.

(*c*) The ultimate product of hydrolysis is dextrose. (The rigid proof of this is much more recent.)

(*d*) The oxidation of cellulose yields oxycellulose, which is markedly acidic.

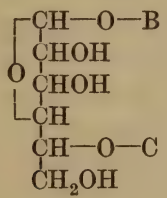
The proof of the chemical constitution of cotton cellulose has been given by Irvine and Hirst,[7] based principally on their own work, that of Denham and Woodhouse,[8] and of Haworth and Leitch.[9] The original papers must be read for a detailed account. The methods used were chiefly—

(1) hydrolysis and graded acetolysis (*i.e.* simultaneous hydrolysis and acetylation) of cellulose, and

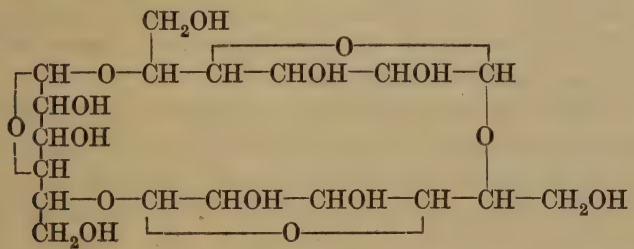
(2) alternate methylation and hydrolysis.

The researches involved identification of the products of these reactions, and careful determinations of the yields in which they were obtained.

It was shown that cellulose contains the dextrose grouping



and next that the residues B and C were also themselves entirely composed of groups having the dextrose configuration. There are several ways in which such a structure might be built up, but Irvine prefers the symmetrical formula :—



It may be noted that one step in the proof depends on the isolation from cellulose by Haworth and Hirst of a crystalline derivative of a sugar containing two C_6 groups in the molecule (cello-biose). It will be seen that Irvine's formula could only yield one molecule of a cello-biose (C_{12}) from one unit (C_{18}) of cellulose, and calculation shows that the *maximum* yield of cello-biose from cellulose would

be 70%. The highest recorded yields are 50—60%, and a yield of more than 70% would disprove Irvine and Hirst's symmetrical C_{18} formula. Irvine and Hirst exclude the possibility of cellobiose being formed in a secondary reaction by the condensation of two molecules of dextrose.

The formula represents cellulose as possessing three hydroxyl groups for every six carbon atoms. Hence unless cellulose is hydrolysed (with formation of new hydroxyl groups) only three ester radicals can be introduced into each C_6 unit. It may be remarked in passing that two of the hydroxyl groups are present in the form of secondary alcoholic groups, and the other as a primary alcoholic group.[10] The formula does little, however, to explain those properties of cellulose and its derivatives which are of chief interest to the varnish manufacturer. Why, for example, is cellulose, with its high percentage of hydroxyl groups, insoluble in water? Why have cellulose and its esters such a high viscosity in solution? Irvine and Hirst realised these difficulties, and their own words may be quoted. The formula is "the simplest expression of a molecule which, *polymerised in unknown numbers*, would represent cellulose as a chemical entity, but we recognise that any odd number of anhydroglucose residues from three upwards can be arranged so as to fulfil the conditions. Our work gives no indication of the degree of polymerisation undergone by the molecular unit, but the extreme insolubility of trimethyl cellulose compared with the ready solubility of methylated starch, inulin and glycogen points to the idea that cellulose is the most highly polymerised of the polysaccharides." It has been remarked by Dorée that the purely chemical and the colloidal investigations of cellulose have proceeded almost independently, and it is of interest to place next to the foregoing quotation from Irvine the views of some of those who have been chiefly interested in cellulose as a colloid.

W. Harrison [11] suggests that the cellulose fibre itself may be regarded as the molecule. Schwalbe and Becker [12] found that when cellulose is mechanically converted into a mucilage by minute subdivision in water, its power of reducing copper is materially increased, presumably because the mechanical rupture of linkages exposes fresh oxidisable atomic groupings. W. L. Balls [13] by the microscopic examination of sections of swollen cotton fibres was able to show well-defined growth rings, and in a later paper [14] concludes that the wall of the hair is probably a sponge-like structure with free air-spaces. Pierce has measured both the rigidity [15] and the plasticity [16] of the cotton fibre. On the other hand, C. F. Cross [17]

regards the cellulose fibre as resembling a liquid system : " Cellulose (reacts) as a labile complex of groups of varying dimensions representing a state of matter somewhat analogous to that of a solution of a saline electrolyte—that is, it reacts rather as a solution-aggregate than by a succession of molecular combinations; the masses actually reacting following the stoichiometrical ratios proper to the dimensions of these ultimate groups, and retaining their relationships in the aggregate, which is thus progressively modified by the entrance of the new groups."

S. S. Napper [18] regards Cross's suggestion as tending in the same direction as Harrison's, and as being in harmony with the view that cellulose is built up by the condensation of soluble constituents of plant juices. J. Böeseken, J. C. van den Berg and A. H. Kerstjens,[19] from a study of the graded acetylation of cellulose, concluded that if the formula is written as $(C_6H_{10}O_5)_n$, n must be at least 45. Duclaux and Wollmann [20] fractionally precipitated an acetone solution of cellulose nitrate and obtained fractions of identical elementary composition but of such widely different viscosity that they probably represented large variations in molecular size.

Any theory of cellulose structure built up from Irvine and Hirst's formula must take account of these views. The polymerisation of the units during growth must take place in three dimensions, and it is not difficult to imagine that the method of condensation may not be uniform. There may be denser packing of C_6 units in some parts of the same fibre than in others, the density depending on atmospheric conditions during growth, such as temperature and humidity, which would probably influence the degree of internal anhydride formation. On the other hand, we must assume that the structure is sufficiently open to allow penetration of cuprammonium solvent, for example, which under controlled conditions will dissolve cellulose without degradation of the structure, or of nitrating acid which will convert cellulose into its nitrate with comparatively little degradation. It may be that the somewhat conflicting evidence on the yield of cello-biose obtainable from cellulose is due to the fact that the condensation of C_6 groups in the structure proceeds irregularly.

Röntgen Ray Evidence.

For work on the application of von Laue's *X*-ray method to the elucidation of the structure of cellulose, reference must be made to the papers of Herzog and Jancke.[21] These investigators state that cellulose from cotton, ramie and wood all showed evidence of con-

taining a crystalline substance with rhombic symmetry, with ratios $a : b : c = 0{\cdot}6935 : 1 : 0{\cdot}4467$. There is also evidence that the particles are regularly orientated or arranged in the direction of the length of the fibre. The dimensions of the elementary cellulose particle are found to be $7{\cdot}9 : 8{\cdot}45 : 10{\cdot}2 \times 10^{-8}$ cm., and Herzog and Jancke deduce that it contains four dextrose residues, or two cello-biose residues. Irvine and Hirst, from chemical evidence, prefer to assume three dextrose residues, or one cello-biose and one dextrose residue, in the unit.

It should be explained that the terms crystal and crystalline refer here solely to the existence of a repeated regular structure in cellulose, causing it to produce a regular pattern by the diffraction of *X*-rays. The popular criteria of the crystalline state, *i.e.*, visible geometrical uniformity, some degree of hardness, and unscattered reflection of light, are evidently absent.

Significance of Viscosity of Cellulose Ester Solutions.

The most important property of cellulose and its esters from the point of view of the varnish manufacturer is the viscosity of their solutions. This property, which is the inverse of fluidity, is a measure of their resistance to flow. It will be treated more fully in a later chapter, but it is necessary to clear up at this point a misapprehension that may arise. It is often stated that the viscosity of cellulose ester solutions is an indication of a highly polymerised molecular structure, and that degradation of the structure reduces viscosity and *vice versa*. On the other hand, it will be shown later that the same sample of cellulose ester will yield solutions of very different viscosity in different solvents and combinations of solvents. It is natural to ask whether the degree of polymerisation of the structure differs in different solvent media? A full answer to this question cannot be given until the constitution of these colloidal solutions has been cleared up, but it may be taken as certain that the difference in viscosity between solutions of the same sample of ester in different solvents does not indicate a difference in the molecular structure of the ester particles, but in the degree to which they are surrounded and swollen by solvent molecules. It follows that it is not safe to draw conclusions as to structural degradation of cellulose esters from viscosity determinations in any single solvent. To put this perhaps more correctly, it is not safe to deduce a high degree of polymerisation from the fact that a sample of ester has a high viscosity in one particular solvent or mixture

of solvents. From the fact that acetone dissolves a very wide range of the nitrates and acetates of cellulose, it has become almost customary to draw conclusions as to the magnitude of the molecular structure from viscosity determinations in acetone solutions. It would be safer to employ a range of solvents, including aqueous acetone and other binary mixtures, and to base deductions as to the structure on the lowest viscosity measured.

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CHAPTER III

NITRATION OF CELLULOSE

Reaction between Cellulose and Mixed Acids—Specification of Acids—Acid Balance—Conditions of Nitration influencing Solubility—Ratio of Acid to Cellulose—Composition of Acid Bath—Time and Temperature—Preliminary Treatment of Cotton—Necessity for Strict Control—Varieties of Cotton Used—Cotton Specifications—Degree of Nitration—Nomenclature of Cellulose Nitrates—Nitration Plant—Direct Dipping—Centrifugal Nitration—Displacement Process—Nitration of Linters in United States—Removal of Acid—Boiling—Poaching—Bleaching—Drying of Nitrocellulose—Dehydration of Nitrocellulose—Properties and Specifications of Nitrocellulose.

CELLULOSE may be nitrated by nitric acid alone, but in practice a mixture of sulphuric and nitric acid is always used. The process consists essentially in bringing cotton cellulose into contact with the mixed acid, and, after nitration is complete, washing out the acid. The cotton does not alter in appearance during the process, but it gains considerably in weight and becomes harsher to the touch and more resistant to water. It does not dissolve in the acids, so that the rate of nitration is determined by the amount of surface exposed to the acid, and the rate of diffusion of the acid mixture through the cotton hairs. The nitration process takes place according to the typical equation

$$R{\cdot}OH + OH{\cdot}NO_2 = R{\cdot}O{\cdot}NO_2 + H_2O,$$

but this does not express the whole of the conditions. The sulphuric acid plays a much more active part than merely to absorb the water formed during nitration. It certainly reacts with the cellulose, since combined sulphuric acid is always found in the product, and it may be that the nitration process consists partly of a replacement of combined sulphuric acid by combined nitric acid. One of the effects of the sulphuric acid is to act hydrolytically by opening up fresh hydroxyl groups, so that there is always a partial depolymerisation during nitration.

Specification of the Acids.

The acids used are of the usual commercial quality, and specifications usually quote the percentage strength and the specific gravity. The nitric acid should not contain too much nitrous acid, and both acids should be reasonably free from suspended matter and dissolved solids. In practice they cannot be obtained entirely free from dissolved and suspended compounds, chiefly of iron and lead, derived from the materials used in the plant in which they are made.

Acid Balance.

The nitration of cellulose never exhausts the acid bath of its nitric acid, so that the spent acid recovered after the nitration can be " revivified " by the addition of stronger acid and brought up to its original strength ready for use again.

For example, in the preparation of cellulose nitrate of high solubility in ether–alcohol, 140 tons of cellulose nitrate was prepared from 2795 tons of an acid having the following composition :—

H_2SO_4	61·7%
HNO_3	23·7%
H_2O	14·6%

The spent acid recovered from the nitration contained :—

H_2SO_4	60·9%
HNO_3	20·2%
H_2O	18·9%

The revivifying acids available were mixed acid containing :—

H_2SO_4	60·5%
HNO_3	31·8%
H_2O	7·7%

and concentrated sulphuric acid containing :—

H_2SO_4	92%
H_2O	8%

To produce the original weight of nitrating bath of the same composition it is necessary to mix :—

Acid.	Weight.	Containing tons		
		H_2SO_4.	HNO_3.	H_2O.
Spent acid	1717 tons	1045	347	325
Revivifying acids :				
(*a*) Mixed.....	994 ,,	602	316	76
(*b*) Sulphuric acid	84 ,,	77	—	7
Totals	2795 tons	1724	663	408
	Percentages	61·7	23·7	14·6

The subject of acid balance is a very important one, and has been dealt with exhaustively in the Technical Records of the Ministry of Munitions,[1] from which the example given above is taken.

Conditions of Nitration influencing Solubility.

If potassium nitrate is to be made by treating potassium hydroxide with nitric acid, a small excess or deficit of nitric acid is not, speaking qualitatively, a serious matter, since it is easy to obtain pure potassium nitrate from the product. The nitration of cellulose is a much more difficult matter. Cellulose nitrate is not a definite chemical individual, and the composition and properties of the product of nitration depend on a number of factors : (*a*) the ratio of acid to cellulose, (*b*) the composition of the acid bath, (*c*) the time and (*d*) the temperature of nitration. To these factors may be added a fifth, (*e*) the physical state of the cellulose before nitration, for neither is cellulose a definite chemical individual. A variation in any one of these conditions leaves its permanent impress on the properties of the cellulose nitrate produced.

(a) *Ratio of Acid to Cellulose.*—Cotton is a bulky material, and in order to make it as susceptible as possible to the action of acids, it is always nitrated in a very open condition. A large quantity of acid is therefore necessary if only to bring all the cotton in contact with acid, and the ratio of acid to cotton in practice varies from about 30/1 to 50/1. Since nitration only takes place in comparatively strong acid mixtures, a considerable excess of acid is always used, and the cellulose nitrate comes into some kind of equilibrium with the spent acid. It follows that if a still higher ratio of acid to cellulose is used, the final cellulose nitrate will be in equilibrium with a stronger spent acid and will therefore be more highly nitrated. The literature of nitration would have been much simplified if it had always been recognised that the degree of nitration depends on the final equilibrium and not on the original strength of the nitrating bath.

(b) *Composition of Acid Bath.*—Numbers of researches have been carried out to trace the influence of the composition of the acid bath on the properties of the cellulose nitrate produced [2-6]. The percentage of nitrogen increases with the strength of the acid bath, *i.e.* roughly speaking, as the proportion of water in the acid bath rises, the percentage of nitrogen taken up by the cellulose falls. In all acid baths used on the large scale, the percentage of sulphuric acid exceeds that of nitric acid, and under these conditions the viscosity of the cellulose nitrate increases with increasing nitric acid content in the bath. The composition of a typical bath for producing cellulose nitrate with high solubility in ether–alcohol has already been given.

(*c*) and (*d*) *Time and Temperature.*—These factors are conveniently considered together. The time of nitration must not be unduly curtailed, as time is necessary for the complete penetration of the cotton hairs by the acid mixture. As far as the combination with nitric acid is concerned, as shown by determination of nitrogen percentage, there is little to be gained by prolonging nitration beyond half an hour. Extra time spent in nitration naturally diminishes the output of the plant, but it also reduces the viscosity, and modifies the solubility relations of the product, so that the time of nitration is not fixed by considerations of output alone.

A high temperature also reduces viscosity, but a practical limit is placed to the employment of this factor by the tendency of the cellulose to oxidise if temperature is too high. This occurrence is known as "fuming off" and leads to the total destruction of the cellulose, and the loss of a considerable quantity of nitric acid in the form of oxides of nitrogen.

(*e*) *Cellulose Purification.*—The purification of cotton for nitration consists chiefly in treatment with hot alkali solutions in closed vessels. Sometimes a bleach is also given. Either treatment if carried too far will begin to break down the cellulose structure and reduce its viscosity. Cellulose from wood yields in general less viscous esters than those from cotton.

Need for Strict Control.

It will be evident from the preceding paragraphs that in order to manufacture cellulose nitrate of uniform quality, strict control must be exercised over the properties of the original cellulose, the composition of the acid bath and all the conditions of nitration. Even when all this has been done, small variations will occur, perhaps the most difficult factor to control being the temperature in the interior of masses of reacting cellulose. These variations must be averaged by careful blending at a later stage of the manufacture.

Cellulose for Nitration Purposes.

In the early days of the manufacture of cellulose nitrate for explosive purposes, several disasters occurred owing to the insufficient stability of the product. One explanation advanced to account for these explosions was the presence in the nitrated cotton of unstable nitro-derivatives of impurities in the original cotton. To diminish the danger from this source, cotton in the purest available form, namely, hanks of yarn, was adopted as the raw material. Researches by Abel [7] in the 'sixties and 'seventies proved that if

the nitrated cotton were pulped, the purification effected by the washing process was greatly improved, and with the introduction of this process it was found possible to employ cotton waste from the spinning mills in place of the expensive hanks of yarn. The utilisation of cotton waste from the spinning mills is an industry in itself, and new methods of treating it were and are continually being discovered.[8] Hence the cellulose nitrate industry has always had to contend with difficulties arising from variations in the quality of its principal raw material. Cellulose nitrate for explosive purposes, when the very highest stability is required, is made from sliver (waste made at the card, comber and draw frames) and from cop bottoms (the last portion of spun thread remaining on the spindles). For the preparation of varnishes, linters (the short hairs remaining attached to the cotton seed after the long hairs have been removed) are largely used, especially in the United States.[9] Lastly, there are the mixed waste swept up in the cotton mills, which contains miscellaneous dirt and oil, and hull fibre,[10] which consists of the short hairs left on the seed after removal of the linters, and is obtained from the seed by the processes known as decortication and defibrination. All these materials require preparation before they can be used for nitration, and the greater the impurity the more drastic the treatment must be. In general, it consists of an alkali boil under pressure, thorough washing with water, sometimes a bleach, followed by acidification and washing again.

Important factory investigations on the preparation of cotton for nitration were carried out during the war, and have been described by Punter.[11] It was found that treatment with dilute alkalies under pressure tended to bring cellulose, derived from several different sources, down to an approximately constant entity yielding solutions of approximately uniform viscosity. By applying the results obtained to the treatment of cotton supplied to explosives factories during the war, it was possible to obtain a much more uniform output from the cordite machines, and to economise in the consumption of the ether–alcohol used as solvent.

In the celluloid industry, cotton cellulose is frequently nitrated in the form of a uniform cotton tissue paper, which is capable of undergoing a very uniform nitration owing to the rapid and thorough manner in which it comes into contact with the nitrating acids.

Wood cellulose has been nitrated for explosives purposes in Germany. It does not give a nitrate of so good a colour as cotton cellulose, but it may find application in the varnish industry. It is usually nitrated in the form of tissue.

Cotton Specifications.

A typical specification may be quoted from Piest, Stich and Vieweg.[12] The cotton must be clean and white. It must not contain impurities such as sand, paper, untorn threads, knots or seed. It must be very loose and suitable for nitration without further treatment. It should not contain much dust, and the fibre must be long and not overbleached. Moisture must not exceed 9%, fat content 0·5%, ash 1% and wood gum 2%. It must not contain more than traces of chlorine. One gramme of the cotton pressed lightly by hand must sink in water within three minutes.

Schwarz [13] gives the following specification: Maximum ash 0·6%, fat 0·4%, water 6%. A white colour, freedom from chlorine, acidity, dust and vegetable impurities.

In considering these and similar specifications it must be remembered that cellulose is not a chemical individual, but a residue which has resisted certain chemical treatments in the course of its manufacture (*i.e.*, alkaline boiling, acidification and possibly bleaching). It is required for its properties as a colloid. It would be useless to specify that it must agree with a certain elementary analysis, since that would give no information about its suitability for the manufacture of esters possessing the required physical properties. The specifications given deal only with possible impurities, for the following reasons:—

Moisture.—Cellulose is hygroscopic and absorbent, and a limit to the moisture content must be fixed for commercial reasons. Moreover, a high avidity for atmospheric moisture often denotes degradation of structure resulting from too drastic purification, while the nitration of damp cellulose increases the evolution of heat and the risk of fuming-off.

Ash.—The mineral matter in cellulose is partly derived from the original inorganic content of the cotton hairs, partly from the water and alkali used in the preliminary treatment, and partly from adventitious impurity. The limit imposed is a safeguard against artificially weighted cellulose and faulty pre-treatment.

Fat.—This is usually termed, more correctly, ether extract. Greasy, oily and resinous impurities may be derived from the original cotton or from external contamination. If from the former, the hot alkaline treatment of the cellulose has been insufficient. These impurities hinder the wetting of the cellulose by the acid, and may leave unstable nitro-bodies in the product. The time of

sinking in water is a rough but useful factory test for the same impurity.

Additional tests frequently agreed between buyers and sellers are the copper number,[15] staining tests,[16] *e.g.*, with a solution of methylene-blue, and determinations of loss of weight on boiling with alkali under specified conditions. The exact significance of some of these tests is not yet completely understood, but they indicate the extent to which reducing and acidic groups have been produced in the cellulose structure, and they can frequently be correlated with the behaviour of the cellulose after its conversion into nitrate.

The most valuable test of cellulose for the varnish manufacturer is undoubtedly its viscosity. Cellulose is dissolved by cuprammonium solution, and a method has been worked out by Gibson, Spencer and McCall [17] for standardising the procedure, and obtaining comparisons of the viscosity of cellulose from different sources. They also showed that the viscosity of esters prepared from cellulose under controlled conditions is governed by that of the original cellulose. Varnish manufacturers would probably prefer in most instances to carry out viscosity determinations on the ester instead of the cellulose, since the procedure is simpler and the results can be directly translated into factory practice. Nevertheless, occasions may arise when the application of a direct viscosity test to the cellulose may be of great value.

Degree of Nitration and Nomenclature.

It has already been pointed out that although theoretically cellulose should be capable of nitration in three distinct stages corresponding to the mono-, di- and tri-nitrate, in practice it is found from the determination of nitrogen percentage that the composition rarely accords with any one of these stages. It is customary therefore to classify cellulose nitrates according to the amount of nitrogen which they contain, and the terms mono-nitrate, etc., have been largely abandoned. The classification by nitrogen percentage has one great advantage in that it indicates roughly the degree of inflammability of the material, those with high nitrogen percentages, *e.g.*, from 12·4 to 13·0%, being the varieties used as explosives. Its disadvantage lies in the fact that it tells nothing of the other properties of the material. Hence a rough and exceedingly arbitrary nomenclature has come into existence in the industry, and it must be emphasised that it rests on no scientific basis and is characterised

by no sharp limits. The range of commercial cellulose nitrates is as follows :—

Nitrogen Percentage.	Names and Uses.
10·2–11·2%	Sometimes called xyloidin in England. Pyroxylin in U.S. Characterised by solubility in camphor–alcohol. Some of the new low-viscosity nitrates said to have nitrogen as low as 11·0%.
11·2–12·4%	Collodion cotton, nitro-cotton, pyroxylin. Chiefly used for lacquers and enamels. High solubility in ether–alcohol. Cellulose nitrate used in service cordite during latter part of war had about 12·2–12·4% nitrogen.
12·4–13·0%	Guncotton. Characterised by diminishing solubility in ether–alcohol as nitrogen content rises, but still soluble in acetone.

Nitration Plant.

The conditions to be satisfied as far as practicable in any plant for the treatment of cellulose with nitrating acid are as follows :—

(1) It should ensure thorough contact between the cellulose and the acid.

(2) It should be adapted to maintain the acid balance between spent and revivified acid, with minimum loss of acid.

(3) Fumes should be minimised, with the object of diminishing the discomfort to the workers, reducing losses of acid, and avoiding the corrosive effect of the fumes on other plant and fittings.

(4) Output should be high, so as to reduce labour charges.

(5) Repairs should be low.

Obviously, in all nitration systems, a compromise has to be made between these conditions when they come into conflict.

For a detailed account of processes of nitration the literature must be consulted. A good description is given by Nathan.[18] The methods may be roughly classified as follows :—

(1) Nitration in pans by direct dipping of the cotton in the acid.

(2) Nitration in centrifugals.

(3) Nitration by displacement process.

(1) Nitration by direct dipping is historically the oldest process. A weighed quantity of cotton is immersed portion by portion in a

measured quantity of the mixed acid. Special precautions are taken to withdraw fumes from the workers, who wear protective clothing and sometimes hoods supplied with compressed air. The bulk of the acid may be removed by hydraulic pressure, but more frequently by spinning in a centrifugal machine. The resulting mass is then quickly drowned by sudden immersion in a large quantity of water.

The chief disadvantages of this method are low output, occasional fuming-off, a great deal of acid fume to be dealt with by ventilation and somewhat heavy repair and replacement charges.

(2) A logical development from the last system is nitration in the centrifugal itself, so as to avoid the transfer of the cotton and acid from the dipping pans to the centrifugal. This process was developed chiefly in Germany. It gives a high output per man, and therefore a low labour charge. The capital cost of the plant is high, and repairs somewhat heavy, as the machines are working in a very corrosive atmosphere.

(3) The displacement process was developed very considerably during the war to supply nitro-cotton soluble in ether–alcohol for cordite manufacture. The fundamental difference between this process and those previously described lies in the manner in which the cotton is freed from acid after nitration. Instead of a sudden drowning of the mixture of acid and cotton in a large volume of water, an extremely slow displacement is effected, by allowing water to flow in slowly at the top of the nitrating pan while the spent acid is withdrawn at the same rate below. The aim in each process is the same, namely, to remove the acid from the cotton without the great rise in temperature which occurs when a strong nitrating acid is mixed with a moderate quantity of water. The displacement process is carried out in wide, shallow earthenware pans. The measured charge of acid is first introduced, and the cotton in as bulky and open a condition as possible is fed in slowly by hand and pushed under the surface with a fork. While this operation is proceeding, the pan is covered with an aluminium hood connected to a fume draught. After the cotton has all been introduced and packed as evenly as possible, perforated earthenware plates in segments are carefully placed on top of the mass so as to cover the whole surface and a small quantity of cold water is allowed to run gently over the plates. If the ratio of acid to cotton, the original mechanical preparation of the cotton, and the packing of the pan are correctly judged, the acid should meet the water layer at a level between the upper and lower surfaces of the earthenware covers,

i.e., in the perforations, so that the actual surface of contact of the water and acid is at a minimum. As soon as the film of water covers the plates, all fuming from the acid is prevented, and the hoods may be removed. The time of nitration may vary from one to four hours, according to the properties desired in the product. When nitration is completed, acid is slowly drawn off at the bottom of the pan and water is run in at the same rate above. The density of the acid is 1·6 to 1·7, so that there is little tendency for the acid and water to mix, and the acid is slowly displaced by the water. The composition of the spent acid issuing below is checked by means of a hydrometer, the readings of which remain practically constant until the zone of acid and water, which results from a slight mixing of the layers, reaches the discharge pipe. This zone can also be recognised by its higher temperature. The strong spent acid is collected in one set of receivers, and a proportion of the weak spent acid in another. The point at which the collection of weak spent acid is stopped is fixed by the economical consideration of whether it pays to recover the acid.

The following advantages are claimed for the displacement process :—

(1) *Economy of Acid.*—The recovery of acid is more complete than is obtained by the use of centrifugal wringing or by hydraulic pressure. It is usual to revivify the greater portion of this, and to return the rest to the acid plant to be treated for the recovery of the nitric and sulphuric acid which it contains.

(2) *Output.*—This naturally depends on the time of nitration, but it compares favourably with the output of the other processes (except the centrifugal process) making the same product. The following figures are given by Nathan :—

Output per Man per Week.

Abel process (Waltham Abbey)	458 lb.
Direct dipping (Ardeer) . .	1112 lb.
Nitrating centrifugal . .	(3000) lb. (Marshall)
Displacement (Waltham Abbey)	1742 lb.

The number of hours worked per week is not stated, but is presumably the same for each process.

(3) There is no handling of acid nitro-cotton. The acid is removed in the original nitrating vessel and the final product is wet with water only.

(4) The loss of nitro-cotton and acids by fuming-off is much diminished.

(5) There are savings in power, water and repairs. On the other hand, the initial capital cost of the plant is high, and the full advantage of acid economy cannot be realised unless the process is used in conjunction with plant for treating the excess of waste acid.

Kirkpatrick has given an interesting description of the purification and nitration of linters for lacquer manufacture. The bales of linters are opened, broken up, teased and freed from dust. The cotton is then blown into autoclaves, in which it is boiled with a dilute alkali solution, the final conditions being a two-hour boil at 100—110 lb. pressure maintained with live steam. The product is thoroughly washed, then bleached under carefully controlled conditions, acidified and washed again. The purified cotton is dried down to a moisture content of $1\frac{1}{2}\%$, and in this condition it is nitrated. The nitration plant is a development of the direct dipping method. The nitrating pans are steel drums with conical bottoms, $2\frac{1}{2}$ ft. in diameter and 4 ft. in depth. Each is stirred by revolving paddles. 35 lb. of cotton are nitrated with 1500 lb. of mixed acid for 25 to 30 minutes. The charge is then tipped into a centrifugal machine to remove the bulk of the spent acid, which is collected and revivified for future use. The remainder of the acid is removed in a drowning vat.

Removal of Acid from Nitro-cellulose.

The stability of nitrocellulose depends almost entirely on the completeness with which it is purified after nitration. There are two sources of acidity which may give trouble, (*a*) acid held mechanically in the cotton; (*b*) sulphuric acid chemically combined with the cellulose as a sulphuric acid ester. The former may be entirely removed by repeated washing with cold water, preferably a hard water containing calcium and magnesium bicarbonates. The removal of free acid from the interior of the fibres is a diffusion process involving time, and the washing must not therefore be unduly hurried, even if the expenditure of water remains the same. For many purposes, a nitro-cotton so purified is sufficiently stable, particularly if it is to be used in enamels containing basic pigments such as zinc oxide. If, however, the highest stability is required, it is necessary to remove the greater part of the combined sulphuric acid also. The combination between the sulphuric acid radical and cellulose is not a stable one, particularly in the presence of traces of moisture and in a warm atmosphere. Free sulphuric acid is slowly liberated, and this has a hydrolysing action on the

nitric ester, liberating nitric acid and weakening the film. The removal of combined sulphuric acid is carried out by boiling with several changes of water. The combined nitric acid is scarcely affected by this process of the reaction if the water is kept slightly acid. The boiling process has long been used in the stabilisation of gun-cotton,[18] but was first put on a scientific basis by the researches of Robertson.[19] It may require local modifications depending on the hardness of the water supply and the amount of combined sulphuric acid to be removed, the latter depending again on the kind of cellulose nitrated and the composition of the acid-bath.

The boiling process is followed by a cold washing process to ensure the complete neutralisation of the liberated acid. It should be noted that the boiling process has a marked influence on the solubility relations of nitro-cotton and tends to make it less viscous.

Washing is carried out in vats resembling the poachers used by paper-makers. These are provided with a revolving drum furnished with knives bearing against similar knives on a bed-plate, so that the nitrocellulose is circulated, and at the same time cut up. A poacher may deal with a large charge of nitro-cotton—five hundredweight or more—and therefore effects a blend of a number of separate nitrations. For varnish manufacture this blending is sufficient. In the manufacture of explosives, blending must be carried further, since the uniformity of explosive power depends on keeping the percentage of nitrogen constant.

Bleaching.—For most purposes it is unnecessary to bleach the nitrocellulose, but if a nearly colourless lacquer is required, it is advantageous to bleach with bleaching powder solution in a faintly acid solution. The excess of bleach is usually removed with sulphurous acid, followed by a thorough washing.

Removal of Water: Drying and Dehydration.

The bulk of the water in the wet cotton so obtained is wrung out in simple centrifugal machines, yielding a product containing usually from 35—40% of water. If the nitro-cotton is to be transported to a distance before use, it is usual to pack it in this form, which is recognised by the railway companies as safe.

The complete drying of the nitro-cotton is a somewhat dangerous process. It is carried out in stoves heated to a temperature of about 40° C., and ventilated to carry off the moisture-laden air. Factories carrying on this process come under the provisions of the Explosives Acts, and the most stringent safety precautions must be taken.

Fortunately for the cellulose nitrate varnish industry, alcohol is a constituent of all the ordinary varnishes, and nitro-cotton may be dehydrated in safety by means of alcohol. The process is essentially the same as the displacement nitration process, since water is displaced from the wet cotton by the lighter liquid alcohol. There are several variants of the process. Nitro-cotton for cordite (R.D.B.) was dehydrated during the war in the Dupont press, by passing a stream of alcohol under pressure through a mass of damp nitrocellulose in a hydraulic press, the spent alcohol passing away through perforations in the face of the lower ram. This process is much quicker than displacement under atmospheric pressure, or under the usual low pressure of compressed air, and is economic in alcohol. Another method is by spraying with alcohol in a centrifugal machine, but this needs a larger quantity of alcohol. In all of these processes, the spent alcohol is collected, and redistilled to bring it up to its original strength for re-use, and in passing it may be mentioned that this process may not be carried on except under the supervision of officers of the Board of Customs and Excise.

The requirements of the varnish manufacturer in regard to dehydration are that the water shall have been effectively removed and replaced by alcohol of such a strength that the nitro-cotton will dissolve in the chosen solvents and film without blooming. The amount of alcohol present in the material must, of course, be taken into account when weighing the nitro-cotton and measuring the liquid ingredients of the varnish.

Description of the Dehydrated Nitro-cotton.

Nitro-cotton made by the above processes closely resembles the original cotton, but the fibre is shorter and feels harsher. It has a tendency to ball together into "pills," which, however, are easily opened out again. The properties of chief interest to the manufacturer, and those which are usually incorporated in a specification, are the following :—

(1) *Solubility.*—This is measured in a specified solvent or mixture of solvents. If, for example, butyl acetate solutions are of most interest to the manufacturer, he may specify a certain maximum quantity of insoluble matter in a solution in butyl acetate of given concentration. When the solvent specified has a high boiling point such as that of butyl acetate, the amount of insoluble matter is determined usually by centrifuging the solution for a certain time

under defined conditions, and measuring the volume of insoluble matter thrown down to the bottom of the tube. If the solvent is readily volatile, a determination can easily be made of the actual amount of nitro-cotton in solution, by evaporating a measured volume to constant weight or by weighing the insoluble residue. The centrifugal method is quicker.

(2) *Viscosity.*—This property is measured at a standard concentration in a specified liquid at a definite temperature, either by

(*a*) measurement of the rate of flow in a capillary tube, or
(*b*) by the rate of fall of a small steel ball in a column of the liquid.

Method (*a*) is most suitable for a highly fluid solution (low viscosity), since the rate of flow of viscous solutions in a capillary tube is so slow that the measurements take too much time. Method (*b*), on the other hand, is difficult to apply with accuracy to a fluid solution, since the time of fall is too rapid to be measured with accuracy, but it is admirably adapted to viscous solutions. It is desirable that measurements of viscosity should be made in solutions approaching as nearly as is practicable the concentrations of the finished varnishes. Hence, in general, the falling sphere is to be preferred to the Ostwald instrument for technical purposes, and it is rather surprising that the British Engineering Standards Association should have adopted the Ostwald viscometer in its specification.

In addition to the obvious limitations as to moisture content, ash and acidity, the following properties may also be specified.

(3) *Stability.*—Imperfectly purified nitro-cotton tends to become acid on keeping, and although in the varnish trade (unlike the explosives industry) this defect is not attended with danger, it is nevertheless often desirable that a maximum rate of decomposition should be fixed. This is particularly so when the varnish films are required to withstand severe atmospheric conditions, but it is also advantageous when the varnish is to be used in contact with any metals, either as a protective lacquer, or as a medium for applying metal powder.

Several methods of testing the stability of cellulose nitrate are known. Since even the most unstable product is very lasting at ordinary temperatures, the tests are always applied to the nitro-cotton heated to a somewhat high temperature, and the assumption is made that the stability at this high temperature affords an estimate of the stability, or the length of useful life, at ordinary

temperatures. The two commonest tests are the Abel heat test, and the Bergmann and Junk test.

The Abel heat test depends on the fact that when cellulose nitrate is exposed to a temperature of 170° F. (76·7° C.) it is slowly decomposed and evolves nitrous fumes. The time is taken for these fumes to reach a concentration at which a piece of moistened filter-paper treated with starch and potassium iodide and suspended in the tube containing the sample, first begins to show discoloration. The significance of the heat test was discussed by Robertson and Smart in 1910,[20] and the method of conducting the test is described in the " First Report of the Departmental Committee on the Heat Test as applied to Explosives " (1914).

The Bergmann and Junk test originated in 1904.[21] In this test the nitro-cotton is heated to a much higher temperature (132° C.) for two hours, and the acid fumes evolved are collected in water and estimated. In the original form of the test, the amount of nitrogen in the water was determined by what is known as the Schultze-Tiemann method. The British Engineering Standards Association have adopted the test, but estimate the collected nitrogen acids by a simple acidimetric titration.

(4) It has already been mentioned that the instability of nitro-cotton is greatly increased by the presence in it of combined sulphuric acid, and that the efficacy of the boiling process as a stabilising agent depends on the reduction in the percentage of this ingredient. Hence an additional but indirect stability test is made by determining the amount of sulphur in the nitro-cotton. This is carried out by oxidising a weighed quantity with nitric acid and potassium or sodium chlorate, and precipitating the sulphuric acid thus produced as barium sulphate. The B.E.S.A. limit for nitro-cellulose for aircraft dope is 0·1% (calculated as H_2SO_4). For varnish for ordinary purposes, the limit need not be so small, and often no limit is specified.

(5) Although the nitrogen content of nitro-cotton has no bearing on its usefulness as a base for varnish, it is a useful check against irregularities in nitration and is so easily applied that it should not be omitted. The best method of determination is the measurement of the nitric oxide evolved when the sample is boiled with a solution of ferrous chloride in hydrochloric acid (Schultze-Tiemann). Perhaps the most widely-used method is that of Lunge, in which is measured the volume of nitric oxide evolved when the sample is shaken with mercury and sulphuric acid. Details of both methods are given in standard books on analysis.

The B.E.S.A.[22] specification for nitro-cotton for aeroplane varnish is contained in No. 2, D. 8 of Nov. 1921, Par. 6 and appendix. This specification is more stringent than is necessary for ordinary varnish work, but strictness is necessary on account of the very severe conditions to which aeroplane varnishes are subjected.

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CHAPTER IV

ACETYLATION OF CELLULOSE

Reaction between Cellulose and Acetylating Bath—Differences from Nitration Process—Catalysts—Non-inflammable Cinema Films—Low Viscosity of Acetates—War Research on Dopes—Principal Manufacturers and Outline of their Patented Processes—Investigations on Partial Hydration—Acetylation Processes in which the Acetate does not Dissolve—Acetylation Plant—Properties and Specification of Cellulose Acetate.

Cellulose acetate is produced when cellulose combines with acetic acid in accordance with the typical equation of acetylation :—

$$R{\cdot}OH + HOOC{\cdot}CH_3 = R{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O.$$

In order to promote the reaction, it is necessary for a so-called catalyst to be present, and the substance almost always used for this purpose is sulphuric acid. Nominally, its function is to combine with the water produced during the esterification. Actually, as in the parallel instance of nitration, it must play a more important part, and the final product always contains combined sulphuric acid. Further, cellulose cannot be acetylated by acetic acid alone. It is necessary to use the more powerful acetylating agent acetic anhydride. This substance alone is capable of taking up all the water produced in the reaction, which is additional evidence that the sulphuric acid is required for some other purpose.

Differences from Nitration Process.

Although nitration and acetylation are analogous in theory, in practice some important differences are found. The most obvious arises from the fact that cellulose acetate is soluble in the mixture of acetic acid, acetic anhydride and sulphuric acid used for the acetylation. Hence as the cellulose is acetylated it passes into solution, and the final product of the reaction is a viscous mass from which the ester is obtained by precipitation with water. In the next place, the time required for acetylation is much longer than the time required for nitration. Lastly, the composition of the acid bath is very different from that used for nitration, the percentage of sulphuric acid being very much smaller.

Catalysts.

Many substances have been investigated with the object of substituting them for sulphuric acid as the catalyst of the reaction.[1] Sulphuric acid has a strong hydrolytic effect on cellulose, and owing to the slowness of the acetylation process, the cellulose always undergoes a considerable degradation in structure simultaneously with acetylation. One of the principal subjects of research in the manufacture has been to find a means of reducing this degradation

to the smallest limits so as to produce a more viscous acetate. This consideration has not been of much importance in the manufacture of cellulose acetate for solutions, where low viscosity is, within limits, often advantageous, but it has been recognised that the toughness and strength of ordinary celluloid are closely related to the high viscosity of its solutions, and that cellulose acetate is not likely to replace cellulose nitrate in celluloid manufacture until it can be made to give solutions of equally high viscosity.

It has been pointed out [2] that all substances which assist the reaction between cellulose and acetic anhydride are solvents of both components. Perhaps it would be more correct to say that the catalyst is capable of being adsorbed by the cellulose, and is also miscible with acetic anhydride, so that the latter is brought into intimate contact with swollen cellulose, exposing a large surface to acetylation. There is probably also a secondary reaction involved in which the sulphuric acid ester of cellulose is converted into the acetic acid ester. The rate of formation of cellulose acetate is governed, not by the rate of acetylation of the hydroxyl groups of the cellulose, but by the rate of diffusion of the acetylating mixture into the cellulose, which is much slower. Many of the substitutes for sulphuric acid which have been patented are compounds of sulphuric acid in which the hydrolytic action of the acid is presumed to be diminished, *e.g.*, sodium bisulphate, sulphates of organic amines, metallic sulphates such as copper sulphate, chamber crystals (nitrosyl sulphuric acid), sulphonyl chloride. It may be doubted whether the inhibition of the hydrolysing power of the acid does not correspondingly retard acetylation, and the use of sulphuric acid in the manufacture on the commercial scale is believed to be almost universal.

The brief sketch in the first chapter brought the history of cellulose acetate up as far as the important hydration process of G. W. Miles, by which it was proved that the solubility relations of cellulose acetate hitherto known could be entirely modified. In following the subject from this point to the present day it must be constantly borne in mind that the main objective of the investigators and manufacturers up till the outbreak of war was not the development of cellulose acetate varnishes. A much more valuable prize was waiting for the manufacturer who could produce from cellulose acetate a film comparable with the celluloid film which was beginning to be used in such enormous quantities for cinema projection. A more difficult problem still was the substitution of cellulose acetate for cellulose nitrate in the manufacture of celluloid

articles, and it may be remarked parenthetically that few of the patentees of the period seemed to know that celluloid cinematographic films are made from an entirely different variety of cellulose nitrate from that used in celluloid articles; or, if they knew, they did not appreciate the importance of the fact, for one continually meets with the tacit assumption that a variety of cellulose acetate suitable for films would also be adapted to the manufacture of celluloid articles.

The most evident difference between the early varieties of cellulose acetate and the cellulose nitrate used in cinema films lay in the lower viscosity of the former and the weakness and brittleness of the films made from it. Dreyfus is usually credited with having been the first to correlate these two facts, and to realise that in order to obtain a stronger film, a more viscous ester must be made, but the deduction was so obvious that it must have been made by many of those engaged in the celluloid film industry as soon as cellulose acetate appeared on the market. From about 1907, therefore, until 1914, the energies of chemists were bent on producing cellulose acetates of higher viscosity without sacrificing the wider range of solubility which the Miles process had made possible.

After the outbreak of war, the direction of research was gradually altered. It has already been shown how cellulose acetate was needed for the doping of aeroplane wings, and how the manufacture of the ester for this purpose had to be increased enormously. The need for high viscosity was now not so great, as satisfactory dopes could be made from an ester of medium viscosity which would not be suitable for making a celluloid substitute. It is somewhat paradoxical that the cellulose nitrate manufacturers since the war should have directed their efforts to obtaining an ester of low viscosity, which the acetate manufacturers before the war were doing their best to avoid.

Information on the progress of the industry during these periods is almost entirely confined to the patent literature, which is unusually intricate and obscure, fully deserving the caustic comment of Briggs.[3] It will therefore be most informative to give the names of those firms who were actually manufacturing cellulose acetate in quantity at the outbreak of war, and to outline briefly the lines of advance indicated by their patents. According to Drinker,[4] these were :—

In France :—The Société Chimique des Usines du Rhône.
In Germany :—The Bayer Company at Leverkusen.
In Switzerland :—The Cellonite Company (Dreyfus Bros.) at Bâle.

Worden [5] mentions also that small amounts were being made by a firm at Lyons in France, and by another near Boston, Mass., for the manufacture of artificial silk.

The Société Chimique des Usines du Rhône patented in 1911 [6] an entirely novel procedure in acetylation, in which the vapour of acetic anhydride is the active agent. Since the boiling point of acetic anhydride at atmospheric pressure is too high, partial vacuum is employed so that the acetylation takes place at about 50—55°. The cellulose may be either dry, damp with water or with a dilute acid. The patent describes as an example the acetylation of cotton impregnated with sulphuric acid. This is placed in a vessel connected with a condenser, receiver and vacuum pump. The vessel is heated to 55°, while the pressure is reduced to 30 mm. The vessel is then connected with a heated still containing acetic anhydride, which boils under this pressure at 50—55°. The vapour of acetic anhydride passes through the mass of cotton and acetylates it, any excess of anhydride being condensed and collected.

In 1913 the same company patented a process [7] on more conventional lines, in which the cellulose is given a preliminary treatment which recalls the earlier processes in which the cellulose is modified by treatment with mineral acids previous to acetylation. It differs from them in that acetic anhydride is present during the initial treatment. For example, 10 parts of cellulose is soaked for several hours at 30° in a mixture of 60 parts of glacial acetic acid, 4 parts of acetic anhydride, and 0·5 part of sulphuric acid. Twenty-one parts of acetic anhydride is then added, and the cellulose is rapidly acetylated and dissolved. It is recovered by precipitation with water in the usual way and yields an ester soluble in chloroform, very slightly soluble in alcohol, and insoluble in nitrobenzene, acetone or ether. Partial hydrolysis modifies the solubility and may be made to yield esters soluble in acetone.

In 1914,[8] the Usines du Rhône patented a process of acetylation in the presence of trioxymethylene, the treatment with which may either precede or accompany acetylation. For example, 10 parts of cellulose is treated for some hours at 30° with 60 parts of glacial acetic acid, 4 parts of acetic anhydride, 0·5 part of 100% sulphuric acid and 1 part of trioxymethylene. Twenty-one parts of acetic anhydride is added, and acetylation is carried on at 40°.

A variant of this process was patented later in the same year [9] in which the trioxymethylene is first converted into methylene sulphate, by treatment with fuming sulphuric acid, and the methylene sulphate is used as catalyst without the addition of free sulphuric

acid. In another patent in the same year,[10] the process described in F.P. 473,399 (*q.v.*) is modified by the use of a little nitric acid in the preliminary treatment. The product of acetylation is described as a nitroacetate, and may contain, for example, 0·5% of combined nitrogen.

In 1920 another variation of the process was patented [11] in which the preliminary treatment of the cellulose before the actual acetylation is carried out at a lower temperature (25—30°) and with less sulphuric acid present (3—5%). The esters thus obtained are insoluble in chloroform. If partially hydrolysed before precipitation, the ester may be obtained in a form insoluble in chloroform and soluble in acetone, or soluble in ethyl acetate.

The Bayer Company first appear in the patent list in 1901. In their earliest patent [12] they describe the preparation of an ester soluble in alcohol, by acting on a hydrated cellulose with acetic anhydride, acetic acid and sulphuric acid. Later they bought Miles's patent, covering the production of acetone-soluble cellulose acetate by the hydration process. Worden [13] describes an acetylation by this process as follows : 100 parts of dry cellulose is acetylated with a mixture of about 300 parts of acetic anhydride and 400 parts of glacial acetic acid with 5 to 9 parts of sulphuric acid as catalyst. The temperature is first kept at about 40°, but may later rise to 50—60°. After from 36 to 40 hours, the cellulose should have passed entirely into solution and a sample on precipitation should be soluble in cold chloroform, but not in acetone. The partial hydrolysis which is characteristic of Miles's process is then begun, by adding slowly, without interrupting the kneading process, a mixture of 60 to 65 parts of water and 60 parts of acetic acid. The product of the original reaction approximates to a triacetate, *i.e.*, an ester containing three acetyl groups to each C_6 unit. After the addition of water, test samples are taken at intervals. It is found that the solubility in chloroform gradually lessens, while that in acetone increases. The process is stopped when the solubility in acetone is complete. At this point, the solubility in chloroform has diminished until the acetate merely swells in that liquid without dispersing. This process of allowing the cellulose acetate to stand while the hydration and solubility changes are proceeding is usually spoken of as ripening. It may need from 12 to 16 hours at a temperature of 40—50°, and during this time the mass is removed from the kneaders and allowed to ripen in separate vessels, which are not usually stirred. The cellulose acetate so produced yields stronger films than those obtained from a solution of the original acetate in chloro-

form. It should be noted that if the hydration of the acetate is allowed to proceed beyond this stage, the product becomes unaffected by chloroform, and the acetone solution will bear the addition of more and more water without precipitation of the ester.[5]

A variation of Miles's process is described by Bayer in 1906,[14] in which dry cellulose acetate is soaked in hydrochloric acid until it is soluble in acetone.

The course of the hydration process has been investigated by Ost and the results were published in a series of papers in 1919.[15] It is interesting to note that the hydration process bears some resemblance to the stabilising of cellulose nitrate by boiling water, in that combined sulphuric acid is eliminated from the ester with proportionately little disturbance to the combined acetic acid. For example, in one of Ost's experiments, a primary acetylation was allowed to " ripen " with the addition of a little water for four days, during which the combined sulphuric acid dropped from over 3% to 0·17%, and the acetic acid from 57·4% to 50·9%.

Ost classified the cellulose acetates as follows :—

(1) The primary products of acetylation are acetates soluble in chloroform, preferably with the addition of a little alcohol. They dissolve in acetone, but yield unsatisfactory films which cannot be entirely redissolved.

(2) The secondary acetates are derived from the primary acetates by mild hydrolysis (hydration). They are easily soluble in acetone and yield good films which can be entirely redissolved.

He found that the limits of acetone solubility lay between 50·9 and 57·6% of combined acetic acid.

Generalisations on the solubility of cellulose esters are always unsafe, as there are so many factors which can be varied in their preparation. The solubility relations of primary acetates prepared by the later Dreyfus processes do not agree with Ost's conclusions, as they are insoluble in chloroform and can be redissolved in acetone indefinitely.[16] Nevertheless, Ost's work contains much useful information on the influence of various catalysts on the course of the acetylation process, and has thrown much light on an obscure and difficult subject.

In 1910 [17] F. Bayer and Co. describe an acetylation process in which aniline bisulphate is used as catalyst instead of sulphuric acid. This process falls into the category mentioned earlier in the chapter of those in which an attempt is made to depress the

hydrolytic activity of sulphuric acid by combining it with another substance—in this instance an aromatic base.

The Dreyfus patents are the most important of all from the technical point of view. The first patent appeared in 1911,[18] and it has been followed by a long series of patents right up to the present time, dealing with all aspects of the manufacture and utilisation of cellulose acetates. A complete list is given by Worden.[5] The conditions to be controlled are (*a*) the ratio of the weights of acetylating agent and of condensing (or catalysing) agent to the weight of cellulose; (*b*) the ratio of the weight of condensing agent to the humidity of the cellulose, (*c*) the temperature. As an example, the directions in the French Patent 478,023 of H. Dreyfus [19] may be briefly abstracted: A mixture of 300—400 kilos. of glacial acetic acid, 250 kilos. of acetic anhydride and 10—15 kilos. of concentrated sulphuric acid is cooled to below 0°. One hundred kilos. of cotton or paper of normal humidity (3—6%) is stirred into the mixture. After a time the temperature rises to 5—15° and then falls again to 5—10°. The cooling may then be discontinued, and the temperature may be allowed to rise to 15—20°. If it is allowed to rise higher than 25—35°, the viscosity of the product will be diminished. Cooling is then started again with constant stirring until the temperature of the mass begins to fall, and the mixture is then allowed to stand until all the fibres have disappeared. At this stage water may be added and the mixture allowed to stand in order to modify the solubility of the product (cf. Miles's process). This process is said to produce cellulose acetate of maximum viscosity insoluble in chloroform, and great stress is laid on the accurate observance of the limits of temperature allowed.

Processes in which the Cellulose Acetate does not Dissolve.

Mention should also be made of processes of acetylation in which the original form of the cellulose is preserved. This is achieved by diluting the acetylation mixture with a liquid in which cellulose acetate is insoluble, but which is miscible with the combined acetylating reagents. The earliest patents on this subject are those of Lederer [20] and Mork.[21] Lederer uses carbon tetrachloride as the non-solvent diluent, while Mork uses benzene. This process appears to have at least two great advantages over the usual process in which the cellulose acetate goes into solution. In the first place, the greater bulk of liquid and the greater ease with which the mass can be stirred must greatly facilitate temperature control. In the second place, the spent acetylating bath can be separated from

the acetate without having to use precipitation by water (which destroys any unused acetic anhydride and dilutes the acetic acid). One would expect, therefore, that it would be possible to revivify the spent bath in much the same way as a nitration bath is brought up to its original strength. The process has certainly been used on a commercial scale in the United States and the writer has examined cellulose acetate made in this way which showed excellent solubility. However, the method has not been widely adopted, and there is probably some technical disadvantage attached to it which does not appear on the surface.

Very little information has been published about the plant used in the acetylation of cellulose, nor is it possible to tell from the patent literature what are the processes actually used in the factories. The outline is as follows : The kneading of the cellulose with the acetylating mixture of acetic anhydride, acetic acid and sulphuric acid takes place in bronze-lined kneaders fitted with two shafts bearing curved blades, designed to shear the contents and keep them continuously in motion. The kneaders are jacketed so that either warm or cold water, or refrigerating brine, may be circulated to control the temperature. Although the Dreyfus patents lay great stress on keeping the temperature below certain limits when working for cellulose acetate of high viscosity, this condition is not so important when the acetate is required for the manufacture of dope, and it will be noticed that the Rhône processes do not employ brine refrigeration. If cold acetylation is required, the acetylating mixture is given a preliminary cooling in a copper or bronze vessel provided with coils for the circulation of brine, before it is introduced into the kneader.

The Dreyfus factories are said to employ cellulose in the form of a special cotton tissue paper, and the Usines du Rhône a special long staple cotton.[4] The British Engineering Standards Association [22] specify for cellulose used in the manufacture of cellulose acetate that it must be neutral in reaction and free from starch. It must not contain more than 8% of moisture, 0·5% soluble in ether, 0·5% soluble in water, and it must not yield more than 0·5% of ash. When boiled with 3% caustic soda under specified conditions it must not lose more than 4% in weight.

After the cellulose has dissolved in the acetylating mixture, it undergoes a ripening process, and for this purpose it is transferred to copper or enamelled vessels which are maintained in a room kept at the appropriate temperature, usually from 30° to 45°. When the examination of samples shows that the right degree of solubility

has been attained (which usually means complete solubility in anhydrous acetone), the cellulose acetate is precipitated by pouring it into a large volume of water. This is done in a wooden vat fitted with stirring gear. The aim of this process is to produce a precipitate in as fine a form as possible, so as to facilitate the washing-out of all traces of free acid, and it is difficult to control the conditions so as to avoid the formation of large clots. The liquor now contains the excess of acetic anhydride and acetic acid in the form of dilute acetic acid together with a small percentage of sulphuric acid. This is treated for the recovery of acetic acid, usually as sodium acetate, which can be employed for the manufacture of acetic anhydride or glacial acetic acid. The precipitate of cellulose acetate is thoroughly washed, with a preliminary grinding if there are large lumps in it. It is then separated off by filtration or centrifuging, dried in warm stoves at 40—50° and ground up. It is particularly necessary that the ester should be in a fine condition so as to dissolve more readily.

Properties of Cellulose Acetate.

Cellulose acetate as it usually occurs in commerce is a white and somewhat dusty powder, not entirely free from small, tough lumps which were originally clots formed in the precipitation by water. The product of those processes in which the cellulose is not allowed to dissolve (Mork and Lederer) retains the original form of the cotton. Cellulose acetate, like cellulose nitrate, is much more resistant to water than the cellulose from which it is made.

It can be distinguished from cellulose nitrate by its solubility in a mixture of chloroform and alcohol, or of tetrachlorethane and alcohol, and by the slowness with which it burns when heated on porcelain or platinum.

Several methods have been proposed for the estimation of combined acetic acid, of which the simplest and best is probably that of Eberstadt,[23] although Fenton and Berry [24] prefer Ost's method.[15] Both depend on the saponification of a weighed quantity of cellulose acetate by alkali.

Eberstadt's [25] method depends on the fact that cellulose acetate swells in a mixture of alcohol and water, and in the swollen state is saponified rapidly and completely by caustic alkali. 0·2—0·3 gramme of cellulose acetate is moistened with a small quantity of alcohol, to which 10 c.c. of *N*-alkali is added. The flask is shaken occasionally, and at the end of an hour the excess of alkali is titrated with normal acid.[26]

Alkaline saponifications are preferred by most authorities to the acid methods in which the acetate is hydrolysed by sulphuric or some other non-volatile acid, and the acetic acid distilled off in steam.

Barnett [1] describes another variation of the alkaline method in which the sample is dissolved in acetone, and saponified by shaking it with standard caustic soda in a stoppered flask. He indicates a slight correction due to neutralisation of soda by the cellulose.

Barr and Bircumshaw [27] prefer Barthélemy's [28] method of hot saponification with normal aqueous sodium hydroxide at 85°, stating that they have obtained more concordant results by this method than by older ones, although the results are not necessarily more accurate.

Determination of Sulphur.

The presence of combined sulphuric acid in cellulose acetate has the same detrimental influence on the stability of the ester as it has on cellulose nitrate. It may be determined by oxidising a weighed quantity with aqua regia, or with a mixture of nitric acid and potassium chlorate, and precipitating the barium chloride as sulphate with the usual precautions.

Entat and Vulquin [29] hydrolyse with water under pressure at 125°, and estimate the sulphuric acid by electrometric titration. They state that the percentage of combined sulphuric acid in a good sample should not exceed 0·03%. This is a somewhat stringent limit, as a good sample analysed by Barr and Bircumshaw (*loc. cit.*) contained 0·04%.

Charring Test.

A second useful stability test developed during the war was the determination of the temperature at which charring is first noticed. The charring is chiefly due to the liberation and concentration of liberated traces of sulphuric acid. Barr and Bircumshaw [27] mention the test and it has been standardised by the British Engineering Standards Association.

A third stability test measures the loss of acetic acid when the sample is heated to a high temperature for a fixed time (compare the Bergmann-Junk test for nitrocellulose). In its earlier form,[27] this was carried out by passing air through the acetate and collecting in standard alkali the acetic acid vapour carried off. In its standardised form the sample is heated with water in a sealed tube for a specified time and the acid set free is titrated with standard alkali.

Solubility is determined in a chosen solvent by dissolving the acetate in the ingredients of the solvent under specified conditions, spinning the solution in a centrifuge and reading off the volume of insoluble matter. If volatile solvents are chosen, such as acetone or methyl acetate, the weight of ester in an aliquot portion drawn off from the clear layer after the solution has stood for some hours, may be found directly by evaporation.

Viscosity.

Viscosity is usually the most important property to be measured, and this test is carried out on a solution of fixed concentration in a specified solvent. The British Engineering Standards Association [30] issue specifications for two varieties of cellulose acetate, one described as "Cellulose Acetate" (2D. 6) and the other as "Medium Viscosity Cellulose Acetate" (D. 50). The solvent in each instance is made up from :—

14 c.c. ethyl alcohol,
14 c.c. benzene,
10 c.c. methyl ethyl ketone,
60 c.c. acetone,
2 c.c. benzyl alcohol,

and in this mixture 6 grammes of the sample must be dissolved. The viscosity at 25° is determined in an Ostwald viscometer and must lie between 30 and 40 for "cellulose acetate," and between 15 and 21 for "medium viscosity cellulose acetate," the standard substance being glycerol, which is given a viscosity in empirical units of 100. Barr [31] has investigated the suitability of glycerol as a standard in viscometry and has drawn attention to the precautions necessary to secure uniformity of results.

The other routine tests are those for water content, acidity, ash and filming capacity. They do not call for special comment.

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* Specifications published by the British Engineering Standards Association may be obtained from the Secretary of the Association, 28 Victoria Street, Westminster, S.W. 1, price 2*d.* post free.

CHAPTER V

CELLULOSE ESTER SOLUTIONS: SOME PROPERTIES. PART I

Phenomena accompanying Dissolution—Viscosity—Movement of Liquids in Capillary Tubes—Falling Sphere Viscometer—Dispersion—Solubility Limit—Solvent Power—Temperature Effect—Constitution of the Esters—Disintegration of Structure during Esterification—Fractional Precipitation of Solutions—Dimensions of Cellulose Hydrolysed by Acids—Contrast with Alkaline Treatment—Chemical Constitution of Solvents of Cellulose Esters—Chiefly Carbonyl Derivatives—Cellulose Nitrate in Single Solvents—Baker's Researches on Concentration and Viscosity—Later Researches—Mixed Solvents—Acetone and Water—Ether and Alcohol—Cellulose Acetate in Binary Mixtures containing Acetone—Mardles Researches —Association and De-association of the Solvents—Plastic Flow (Bingham)—The Tyndall Effect.

Colloidal Nature of Cellulose Ester Solutions

Phenomena accompanying Dissolution.

If a small quantity of dry cellulose nitrate or acetate is covered with a suitable solvent, *e.g.*, acetone, the ester rapidly turns to a transparent jelly, which if left undisturbed will remain at the bottom of the vessel almost indefinitely. If the mass is stirred or shaken, the jelly is gradually distributed in the solution until the latter becomes homogeneous to the naked eye, except for small particles of insoluble impurities, such as incompletely esterified cellulose and dust, which are seldom entirely absent from the technical esters. If the solution is centrifuged at an early stage of the mixing, a considerable quantity of undispersed jelly may be thrown down to the bottom of the tube, but as the mixing becomes more complete the amount becomes less, and a well-mixed solution of ester of good solubility when whirled in a centrifugæ will deposit little except the insoluble impurities already mentioned. The features accompanying the dispersion of nitrocellulose in ether–alcohol and acetone in particular are described by Masson and McCall,[1] and a very thorough investigation of the preliminary swelling of cellulose acetate in mixtures of solvent and non-solvent liquids was made by Knoevenagel and his pupils (*v. infra*).

The most noticeable property of the solutions is their increased viscosity when compared with the original solvents. This is roughly demonstrated by tipping or inverting the vessels containing them. The name of "colloid" was originally given by Thomas Graham to those substances which, like glue, form viscous solutions, in which the dissolved substance possesses a very low rate of diffusion compared with crystalline bodies. The cellulose esters form viscous colloidal solutions, known as "sols" (also after Graham), while under some conditions they may deposit some or all of their colloid content as "gels." The nomenclature of colloid chemistry is not

yet quite firmly established, and colloid terms will not be used in this chapter more than is necessary.

Viscosity.

If we imagine two plane surfaces in a liquid, each of unit area (one square cm.), and one centimetre apart, forming as it were two opposite surfaces of a cube of the liquid, it is evident that to keep these surfaces moving relatively to each other, each remaining in its own plane, will require more force in some liquids than in others. The inherent property in a liquid which opposes this motion is called its viscosity, and is defined as the tangential force on a unit area of either of two horizontal planes at a unit distance apart required to move one plane with unit velocity in reference to the other plane, the space between being filled with the viscous substance (Bingham,[2] from Clerk-Maxwell). If the force applied is F, the velocity of one plane relative to the other is v, and their distance apart s, the coefficient of viscosity $\eta = \frac{Fs}{v}$.

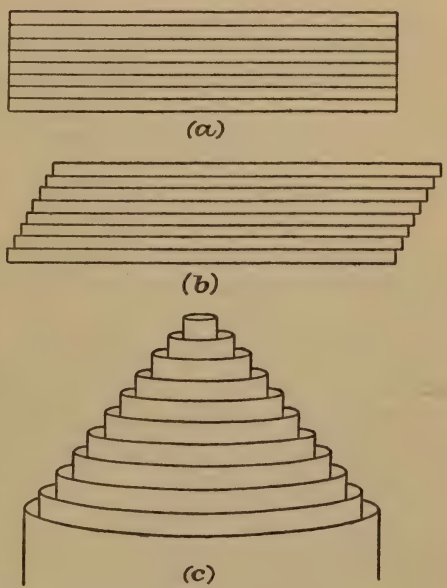


FIG. 1.

The viscosity of a liquid is sometimes called its internal friction, and the analogy with solid friction will be apparent, although it must not be taken too far. The viscosity of cellulose ester solutions increases at a very rapid rate with the concentration, so that in plotting the viscosity–concentration curve it is usual to plot the logarithm of the viscosity instead of the actual number. This has led to the deduction of some interesting empirical equations connecting viscosity and concentration (*v. infra*).

The simplest mechanical illustration of layers of liquid sliding over one another is given by deforming a pack of cards by a shearing stress from the shape illustrated in Fig. 1 (*a*) to the shape illustrated in Fig. 1 (*b*). The experimental measurement of viscosity, however, by a method reproducing the conditions laid down in the definition, would be extremely difficult, and the classic method is by

the movement of the liquid in a capillary tube. It is not easy at first to see how this movement realises the theoretical idea of layers of liquid sliding over one another, but if we take as an illustration, instead of a pack of cards, a rolled-up tape measure, and deform it by pushing the centre out (cf. Fig. 1 (*c*)), we see how the movement of liquid in a capillary tube may be regarded as being made up of a series of *concentric* layers moving relatively to each other, the velocity being zero at the circumference (where the liquid touches the tube) and greatest at the centre.

The equation connecting the radius of the tube, the head of pressure on the liquid, the rate of flow and the viscosity of the liquid is $\eta = \frac{pgR^2}{8lI}$, in which

p = pressure on the liquid.
g = acceleration due to gravity.
R = radius of capillary.
l = length of tube.
I = velocity of flow (c.c. per sec.).

It was derived experimentally in another form by Poiseuille in 1842. Poiseuille's original publications are not readily available, but his results have been republished by Bingham, and should be consulted by all those interested in the subject. The accuracy of the agreement with the derived equation is on the whole remarkable.

The measurement of rate of flow in a capillary tube is still perhaps the most widely used method of determining viscosity. For dealing with solutions of very high viscosity, however, there are more convenient methods. One depends on measurement of the rate of fall of a small steel ball through the solution, and makes use of the original mathematical investigation of Stokes. It was developed for cellulose ester solutions by Sheppard [3] and by Gibson and Jacobs.[4] Others measure the actual friction when one metal cylinder is rotated inside another concentric with it, the space between being filled with the liquid under investigation. Measurements of the viscosity of cellulose esters for technical purposes are usually made either with the Ostwald (capillary tube) (B.E.S.A.) or the falling sphere instruments.

Dispersion.

Strictly speaking, the term solution should be applied only to those mixtures in which the components are subdivided down to molecular limits. Viscous colloids are believed to subdivide into particles much larger than molecules, and they are therefore said to

disperse rather than to dissolve, and to form dispersions rather than solutions. The term "colloid solution," however, it used even in purely scientific literature when the context provides against misconception. It is becoming customary to distinguish between "solution" and "dissolution," the latter referring to the process of dissolving, and the former to the product. "Dispersion" at present carries both meanings, but "spersion" may arrive in due course.

Solubility Limit.

When a crystalline substance, *e.g.*, sodium chloride, is dissolved in water, it is common knowledge that if the quantity of salt is increased, a point is reached at which the liquid, at any fixed temperature, will dissolve no more of the solid. An alteration in temperature will usually cause an alteration in the quantity that can be dissolved, but the limiting concentration is just as sharp. The cellulose esters behave differently. If we continue to add cellulose nitrate to acetone, it will disperse with more and more difficulty owing to the mechanical difficulty of stirring the viscous mass, but we do not reach a point at which the acetone is saturated with cellulose nitrate and cannot dissolve any more. The limit appears to be set only by the mechanical strength of our apparatus. Hence we cannot compare the technical advantages of different solvents of a cellulose ester by measuring the concentration of the ester at saturation point, as we should do if we were dealing with a crystalline substance; other methods have to be used. The most obvious one is suggested by the earlier part of this paragraph. If the dispersion of the ester in the solvent is limited only by the mechanical strength of the apparatus, that solvent is the best (in regard to solvent power only) which at equal concentration gives the least viscous, and therefore most easily workable, solution. Hence one way of comparing solvent power is to measure the viscosity of solutions of the same cellulose ester at the same concentration.

Another method arises indirectly from economic considerations. It is often possible, under conditions which will be discussed later, to dilute solutions of a cellulose ester in a solvent with a cheap non-solvent. For example, a solution of cellulose nitrate in amyl acetate may be diluted with petroleum spirit to a considerable extent without causing precipitation of the dissolved ester. Hence one may compare two solvents, such as, for example, amyl acetate and ethyl acetate, by preparing from each a solution of cellulose nitrate of identical concentration, and determining what proportion

of petroleum spirit may be added to each, at any chosen temperature, before precipitation begins.

Correlation of Solvent Power and Viscosity of Cellulose Ester Solutions.

This experiment determines the " solvent power number," which has been defined by Mardles [5] as the volume in cubic centimetres of a miscible non-solvent required to start precipitation of a cellulose ester from 1 gramme of a 5% solution at 20°.

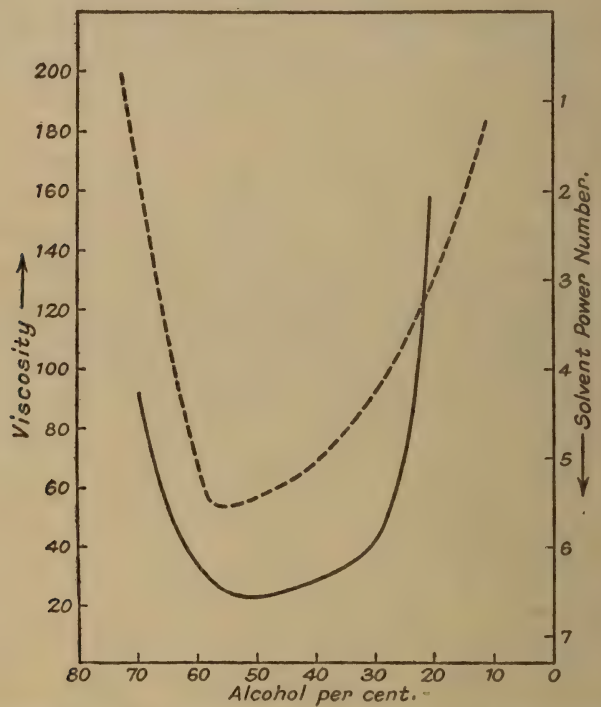


FIG. 2 (Mardles).—The curves connecting viscosity and solvent power number with the composition of the solvent are here plotted for a solution of nitrocellulose in ether–alcohol. Note that each curve displays a decided minimum at approximately 50—60% of alcohol in the solvent, and that viscosity is measured upwards and solvent power number downwards. Thus minimum viscosity corresponds approximately with maximum solvent power, *i.e.*, maximum resistance to precipitation by a diluent.

It has been shown by Mardles [6] that there is a near relation between the viscosity of a solution of cellulose ester and the solvent power, and if these two properties are measured for solutions of cellulose esters in mixtures of two liquids in varying proportions, the curves expressing the results are generally similar in shape, *i.e.*, these two methods of estimating the solvent value of a liquid

usually show moderately good agreement (see Fig. 2). Mardles points out that on theoretical grounds the best solvent mixture should be the least viscous (*i.e.*, the most fluid), since high fluidity indicates a considerable degree of dispersion and therefore a close approach to true solution. The industrial value of these measurements is evident from the fact that the solvents of highest solvent power are those which dissolve the esters most rapidly, and which give solutions of required viscosity with the smallest volume of solvent, while the solutions are the clearest and have the least tendency to coagulate.

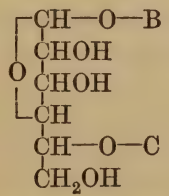
Effect of Temperature.

Although there is no definite limit to the amount of cellulose ester which can be dissolved in a given solvent, there exists for many substances a temperature above which they are solvents and below which they are not. This critical temperature has been termed the transition temperature.[7] It is not quite sharp, probably owing to the heterogeneity of commercial cellulose esters, and it varies slightly with the concentration, so that the concentration of the solution should be stated when quoting it. The usual concentration employed for the determination is 5%. Increase of temperature always lowers the viscosity of solutions.

Chemical Constitution of the Cellulose Esters.

Before considering the results obtained in the investigation of single and mixed solvents, a few words should be said about the constitution of the esters themselves.

It will be recalled that cellulose has been proved to be built up of glucose anhydride residues, having the formula :—



The groups B and C are themselves built up of similar glucose units. This formula contains three hydroxyl groups in every C_6 unit, and we may write it as $[C_6H_7O_2(OH)_3]_n$. These hydroxyl groups may theoretically be esterified in three stages, yielding the compounds

$C_6H_7O_2(OH)_2(OR)$
$C_6H_7O_2(OH)\ (OR)_2$
$C_6H_7O_2(OR)_3$

R being $CH_3 \cdot CO$ in the acetic esters and NO_2 in the nitric esters. In the following table are shown the percentages of hydroxyl group, of acetyl group as acetic acid and of nitryl group as nitrogen in the theoretical cellulose group as the hydroxyl groups are successively esterified :—

	% OH in acetate.	% acetic acid in acetate.	% OH in nitrate.	% N in nitrate.
Cellulose	[31·5]	nil	[31·5]	nil
,, mono-ester	16·7	29·4	16·4	6·8
,, di-ester.....	6·9	48·8	6·7	11·1
,, tri-ester	nil	62·5	nil	14·1

It must be emphasised that these figures refer only to a theoretical esterification in which there has been no simultaneous hydrolysis of anhydride oxygen (—O—) atoms in the cellulose.

Thus the theoretical cellulose di-nitrate contains 11·1% of nitrogen and 6·7% of hydroxyl. The corresponding di-acetate contains acetyl groups equivalent to 48·8% of acetic acid and 6·9% of hydroxyl, while the tri-acetate contains 62·5% of acetic acid and no hydroxyl. It is evident therefore that, except in the instance of completely esterified cellulose, there is sufficient free hydroxyl in the ester to lead us to expect some evidence of its presence in the properties of the material. We know, moreover, that esterification of cellulose is always accompanied by some degree of hydrolysis which increases the percentage of hydroxyl group to more than the theoretical value.

It has already been mentioned that the products of nitration and acetylation of cellulose do not indicate directly the esterification of exactly one, two or three hydroxyl groups. Stable cellulose nitrates may be obtained with any percentage of nitrogen from about 10% to nearly 14%. This has been explained on the hypothesis that the ester groups are not chemically combined with the cellulose, but adsorbed. This theory, however, has had little or no support, and the usual view is that all the C_6 units need not necessarily be esterified to the same extent. Some, for example, may be di-nitrates, others tri-nitrates, the average percentage of nitrogen for the nitrate in bulk corresponding to something between a di-nitrate and a tri-nitrate. Another consideration which has been lost sight of to some extent is that since hydrolysis takes place simultaneously with esterification, the percentage of nitrogen must thereby be altered.

For instance, if an oxygen linkage between two neighbouring C_6 units is hydrolysed by addition of water, simultaneously with the esterification of two hydroxyl groups in each unit, the percentage of nitrogen in the two units considered together will not be 11·1%, as in the theoretical di-nitrate, but 10·4%. This is, of course, an extreme case, but it is evident that some degree of hydrolysis distributed over a comparatively large conglomerate of C_6 units will cause the percentage of nitrogen in a true di-nitrate to diverge appreciably from 11·1%.

Disintegration of Cellulose Structure during Esterification.

We have already seen that the degree of polymerisation of the cellulose unit, or, in other words, the value of n in the formula $(C_6H_{10}O_5)_n$ is unknown. It has been suggested that the entire cotton hair may be a single "molecule" of cellulose, and it must be admitted that the larger the structure grows, the more difficult it is to see what internal forces can suddenly come into play to stop growth. The limit is probably enforced by conditions external to the plant, such as temperature and especially humidity. Thus it has recently been shown [8] that there is a large variation in the viscosity of nitrocellulose prepared from wood cellulose which has been extracted from concentric rings of the same section of the trunk of a poplar tree. The central zone yielded nitrocellulose with the lowest viscosity and the outer zone nitrocellulose with the highest viscosity.

The high initial viscosity of a solution of cotton cellulose which has not been exposed to light or oxidation is attributed by Barr [9] to the existence of an outer cuticle of cellulose more highly polymerised than the rest of the cotton hair.

It is natural to ask to what extent the structure is disintegrated during esterification. It is not likely that, even if the structure of cotton cellulose is coterminous with the cotton hair, it will nitrate as a hair, although experiments are on record in the celluloid industry in which transparent celluloid gradually developed cloudiness due to the appearance of fibres.[10] Prolonged nitration or acetylation always give products of low viscosity, and there is little doubt that hydrolysis and esterification begin simultaneously with the immersion of the cotton in the acids. The product of a nitration probably consists of fragments of the original cellulose, not of uniform size, of which the smaller ones have probably undergone a greater proportionate degree of hydrolysis than the larger. The mental picture of the esterification process is assisted if we

remember that according to Balls [11] the wall of the cotton hair is probably a sponge-like structure containing free air spaces, and therefore presenting a large surface to the esterifying acids.

Fractional Precipitation of Solutions.

The presence of units of different dimensions in cellulose esters is clearly shown by the experiments of Duclaux and Wollman,[12] who fractionally precipitated a solution of cellulose nitrate in acetone by means of aqueous acetone, and found that although the various fractions were practically identical in nitrogen percentage, they differed greatly in viscosity, the earliest fraction (*i.e.*, the first fraction to precipitate) having the highest viscosity, and succeeding fractions diminishing progressively in viscosity. Since it is unlikely that the method of precipitation could have any influence on the molecular dimensions of the dissolved particles, we must conclude that these various cellulose nitrates of different viscosity co-exist in the original solution, and that the least viscous are the most soluble in aqueous acetone. Cellulose acetate has been found in the writer's laboratory to behave similarly.

The acetylation of cellulose has been the subject of interesting research from a similar point of view by Böeseken, van den Berg, and Kerstjens.[13] The formula for cellulose may be written

$$(C_6H_{12}O_6)_n - (n - 1)H_2O,$$

in which n diminishes as the structure is hydrolysed, while the percentage of acetic acid rises from 62·5% for cellulose tri-acetate to 77% (for dextrose pentacetate, *i.e.*, after complete hydrolysis to dextrose). Böeseken and his colleagues first found that if acetylation were stopped before the cellulose had gone into solution, the acetate found in solution was the tri-acetate, and the undissolved cellulose was practically unesterified. They therefore concluded that when acetylation occurred the tri-acetate was formed immediately. When cellulose $(C_6H_{10}O_5)_n$ is hydrolysed by the addition of one molecule of water, its molecular weight becomes $(C_6H_{10}O_5)_n + 18$, and the number of hydroxyl groups becomes $3n + 2$. Hence $3n + 2$ molecules of acetic acid will be required for the acetylation to tri-acetate, and, since one molecule of water is lost for each hydroxyl acetylated, the molecular weight of the product will be given by the formula

$$[(C_6H_{10}O_5)_n + 18] + (3n + 2)(CH_3{\cdot}COOH) - (3n + 2)(H_2O) = [288n + 102]$$

The percentage of acetic acid in this tri-acetate is

$$\frac{100 \times 60(3n + 2)}{288n + 102} \text{ or } \frac{18{,}000n + 12{,}000}{288n + 102}$$

and since this constituent can be determined analytically, the value of n can be found; it gives the average number of condensed dextrose groups in the products of hydrolysis. When n is very large, the percentage of acetic acid in the product closely approaches $\frac{18{,}000}{288}$ or 62·5%. As n becomes smaller, the value approaches 77%. It was found by following the course of acetylation that the experimental number did not rapidly increase above 62·5%, showing that the cellulose had probably at first hydrolysed into fragments approximately equal in size. This was confirmed by the fact that only a small proportion of the product dissolved in ether–alcohol, which dissolves the acetates of the carbohydrates of low molecular weight. When once the increase in combined acetic acid begins, however, it becomes rapid, and indicates that the cellulose structure is being disintegrated quickly.

Barnett [14] found that cellulose acetates contain free ketonic groups which react in the normal way with phenylhydrazine or *p*-bromophenylhydrazine, often forming compounds of definite melting point. By determining the percentage of nitrogen or bromine in these compounds he was able to deduce values for n, which he found to vary from 2 to 12 for the phenylhydrazones and from 9 to 36 for the bromophenylhydrazones. The method is useful for showing progressive degradation of the cellulose structure as the acetylation proceeds, but many of the acetates studied appear to have been considerably further depolymerised than those used in industry.

[It is interesting to compare with these results those obtained by Irvine and Hirst [15] in the methylation of cellulose, in an *alkaline* medium by the method of Denham and Woodhouse. Fourteen methylations yielded a product containing 43·8% OCH_3, and twenty more methylations produced no further rise in the percentage of methoxyl groups. Irvine concluded that methylation caused no hydrolysis or oxidation of the cellulose molecule. With this conclusion may be compared the results obtained by Punter [16] and his collaborators on a very different scale, in the technical treatment of cotton required to produce uniform viscosity. They found that hot alkaline treatment of different varieties caused reduction of viscosity, and therefore presumably of structure, but

after a time all varieties appeared to be reduced to the same more stable structure, the viscosity of which was not altered by further treatment of the same kind, as long as no chemical breakdown took place. Something of the same nature may have happened to Irvine's methylated cellulose in the early methylations, so that the formula which he derived may be that of a cellulose modified by the alkaline treatment.]

The evidence therefore suggests that the acetylation or nitration of cellulose yields a product which consists of fragments of the original cellulose structure, probably not esterified uniformly as regards the number of ester groups in each C_6 unit, not of uniform dimensions, and therefore not uniformly hydrolysed, but perhaps not differing very largely in this respect.

Chemical Constitution of Solvents.

It has been mentioned in the first chapter of this book that the earlier developments of cellulose nitrate solutions were much hampered by the lack of suitable solvents. As soon as it was realised that there were vast commercial possibilities in such solutions, a large number of substances were tested and many of them patented. De Mosenthal [17] gives a long list and Worden [18] one still longer. It has been said quite recently by a critic that the method of research seems to be one of trial and error. There are, however, some regularities which give indications of the constitution and properties which confer solvent power for cellulose esters. Cellulose nitrate is dissolved by the lower ketones, *e.g.*, acetone, methyl ethyl ketone, diethyl ketone; by the methyl, ethyl, propyl, butyl and amyl esters of formic, acetic, propionic and butyric acids; and by various derivatives of acetanilide. Cellulose acetate is dissolved by acetone, methyl acetate, methyl and ethyl formate, formic and acetic acids. We find, however, an extremely interesting class of solvents prepared by mixing liquids which, by themselves, have little or no solvent power. For example, for cellulose acetate: chloroform and alcohol, tetrachloroethane and alcohol, benzene and alcohol (hot). For cellulose nitrate: ethyl ether and alcohol, benzene and alcohol, toluene and alcohol. Since, for technical purposes, cellulose esters are almost always employed in mixed and not single solvents, the investigation of this phenomenon is of great technical interest, and during the war, owing to the shortage of solvents and the imperative necessity of reducing the demands on shipping, the research became a national necessity. If we examine the lists of cellulose ester solvents, we notice that

single solvents always contain some atomic grouping of marked reactivity. Consider, for example, the list of cellulose nitrate solvents given above. These substances are all either ketones, esters, or anilides, the distinctive groupings of which are

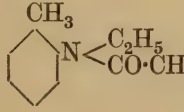
$$\begin{matrix} R_1—CO—R_2 \\ R_1—CO—OR_2, \\ Ar—NH—CO—R_1 \end{matrix}$$

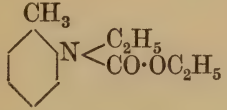
respectively, the carbonyl group —CO— being common to all of them.

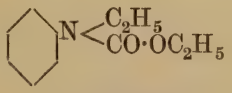
Cellulose Nitrate in Single Solvents.

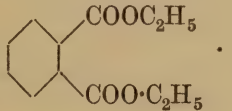
The first systematic examination of single solvents for cellulose nitrate was made by Baker,[19] who studied the relation between viscosity and concentration, using three different typical samples of the material. The solvents used were :—

Acetone, $CH_3 \cdot CO \cdot CH_3$;
Ethyl formate, $H \cdot COO \cdot C_2H_5$;
Methyl acetate, $CH_3 \cdot COO \cdot CH_3$;
Ethyl acetate, $CH_3 \cdot COO \cdot C_2H_5$;
Propyl acetate, $CH_3 \cdot COO \cdot C_3H_7$;
Amyl acetate, $CH_3 \cdot COOC_5H_{11}$;
Ethyl butyrate, $C_3H_7 \cdot COOC_2H_5$;

Aceto ethyl-*o*-toluidide,  (the phenyl analogue is *mannol*)

Ethyl-*o*-tolylethyl carbamate, 

Phenyl ethyl urethane, 

Ethyl phthalate, 

Baker found that if concentration were plotted against viscosity at constant temperature, the curve for each solvent could be represented by the empirical formula

$$\eta = \eta_0 (1 + ac)^k$$

where

η = viscosity of solution at concentration c
η_0 = viscosity of solvent
a, k = constants, different for each solvent.

A convenient expression for comparing different solvents is given by the differential

$$\frac{d \log \eta}{dc} = \text{constant}$$

The value of this constant differs for the same nitrocellulose in different solvents and hence the effect of cellulose nitrate on the viscosity of its solutions varies with the nature of the solvent. Probably also the condition of the nitrate is not the same in different

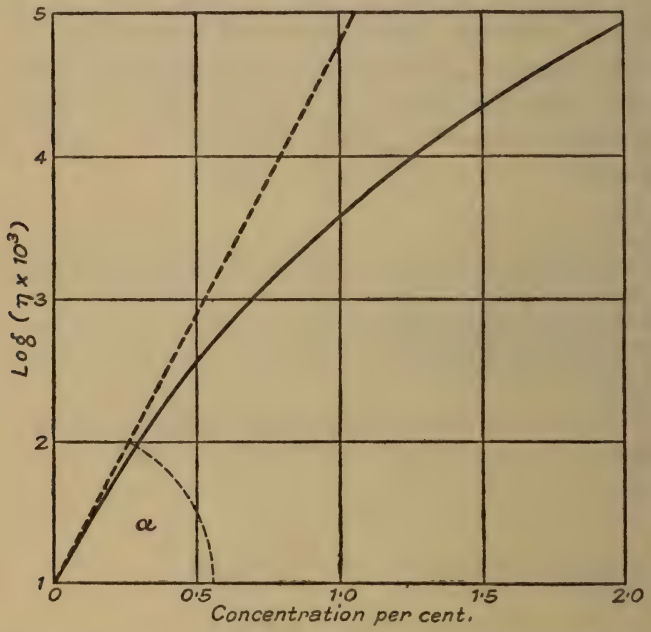


FIG. 3 (Baker).—Concentration of nitrocellulose plotted against the logarithm of the viscosity, for a solution in equal volumes of benzyl alcohol and ethyl ether.

If $\eta = \eta_0 (1 + ac)^k$

Then $\frac{d \log_{10} \eta}{dc} = \frac{ak}{e}$

and $ak = 2{\cdot}303 \tan \alpha$, where α is the angle between the tangent and the concentration axis. The value of ak is a characteristic function of each curve (Baker, *loc. cit.*).

liquids. Hence the act of solution produces some change in the cellulose nitrate other than a merely physical change of state. Baker concluded that the cellulose nitrate becomes associated with the solvent, so that the true solute is not cellulose nitrate, but a complex of cellulose nitrate and the solvent. He accepts a suggestion previously put forward by Schwarz [20] from a study of the viscosity of cellulose nitrate in camphor and alcohol, that the fluidity (*i.e.*, the inverse of viscosity) of a solution of cellulose

nitrate in a solvent is a criterion of the gelatinising or solvent power of the liquid.

Results similar to Baker's were obtained by C. Visser [21] by the examination of cellulose acetate from three different sources in the simple solvents acetone, methyl acetate and ethyl formate. Her equation, which is also derived empirically from an examination of the curves, is of the same form as Baker's, namely,

$$\eta = \eta_0\left(1 + \frac{C}{Q}\right)^P$$

where P and Q are constants, and she adopts the suggestion of Baker and of Hatschek [22] that the aggregates in the solution consist of the dissolved ester combined in some way with part of the solvent, so that the disperse phase is a complex depending on the grade of cellulose acetate and the nature of the solvent. This paper gives a brief discussion of the formulæ suggested by

Einstein (*Ann. Physik*, 1906, (iv), **19**, 289).
Hatschek (*Z. Chem. Ind. Koll.*, 1910, **7**, 301–304; *ibid.*, 1911, **8**, 34–39).
Bancelin (*Compt. rend.*, 1911, **152**, 1382).
Kendall (*Medd. K. Vet. Nobelinst.*, 1913, **2**, No. 25, 1–16).
Arrhenius (*Z. Phys. Chem.*, 1887, **1**, 288).
Baker (*Trans. Chem. Soc.*, 1913, **103**, 1653–1675, *v. supra*).
Smoluchowski (*Koll. Z.*, 1916, **18**, 190).

connecting viscosity and concentration.

Duclaux and Wollman [12] arrived at a still simpler equation connecting concentration and viscosity, namely :—

$$\eta = \eta_0 \cdot 10^{kc},$$

and state that k is almost independent of the solvent for the same nitrocellulose, but differs greatly with different nitrocelluloses so that it forms a kind of index of the viscosity of cellulose nitrate. It will be noted that if the viscosity of a sample of cellulose nitrate is η' in solvent A, and η'' at the same concentration in solvent B, then

$$\eta' = \eta_0' \cdot 10^{kc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$\eta'' = \eta_0'' \cdot 10^{kc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If k is independent of the solvent, we obtain by dividing equation (1) by equation (2)

$$\frac{\eta'}{\eta''} = \frac{\eta_0'}{\eta_0''}$$

i.e., the viscosities of solutions of equal concentrations are in the same ratio as the viscosities of the solvents. This relation would certainly not hold over a wide range of different solvents and different nitrocelluloses, but the results given by Duclaux and Wollman are of considerable interest, and it would be a valuable research to determine the limits of the applicability of the equation. If it was derived only from the examination of the products of the fractional precipitation of solutions of cellulose nitrate in acetone, it suggests that these fractions may show regularities (perhaps due to more restricted range of dimensions) which are not shown by samples derived from entirely different processes of nitration.

Cellulose Esters in Mixed Solvents.

Cellulose Nitrate in Acetone and Water.

This system was examined by Masson and McCall,[1] who found that the viscosities of solutions in anhydrous acetone are comparatively high, but are lowered by the presence of small quantities of water. A minimum value exists which corresponds to a percentage of water which is slightly different for different samples of nitrocellulose, and also varies somewhat with the concentration for the same samples of nitrocellulose (see Fig. 4). For example, using cellulose nitrate containing 12·3% of nitrogen, the minimum viscosity for a 5% solution occurs at 8—9% of water, and for a 10% solution at 9—10% of water. Using cellulose nitrate containing 13·0% of nitrogen (gun-cotton), the minimum viscosity for a 5% solution occurs at 6—7% of water and for a 10% solution at 7% of water. If the amount of water is increased much beyond these figures, a point is reached at which gelatinisation still occurs, but the cellulose nitrate will not disperse.

As a matter of interest it may be mentioned that at still higher concentrations of water a mixture is reached which when shaken with fibrous cellulose nitrate will powder it without dissolving it (although a small loss of weight occurs). This process is an approach to the fractionation process of Duclaux and Wollman [12] from the opposite direction.

Ether and Alcohol.

When it is found that certain varieties of cellulose nitrate dissolve in a mixture of ether and alcohol, neither of which is a solvent alone at ordinary temperatures, nor contains an atomic grouping which would lead us by analogy to expect that it would

be a solvent, it is natural to speculate whether, when the two solvents are mixed, any complex is formed which rearranges their affinities. Baker [23] investigated pure ether–alcohol mixtures from this point of view, using the sensitive property of viscosity as a test for complex formation. He concluded that mixtures of alcohol and ether contain

(*a*) non-associated ether,
(*b*) ether–alcohol complex,
(*c*) non-associated alcohol,
(*d*) associated alcohol,

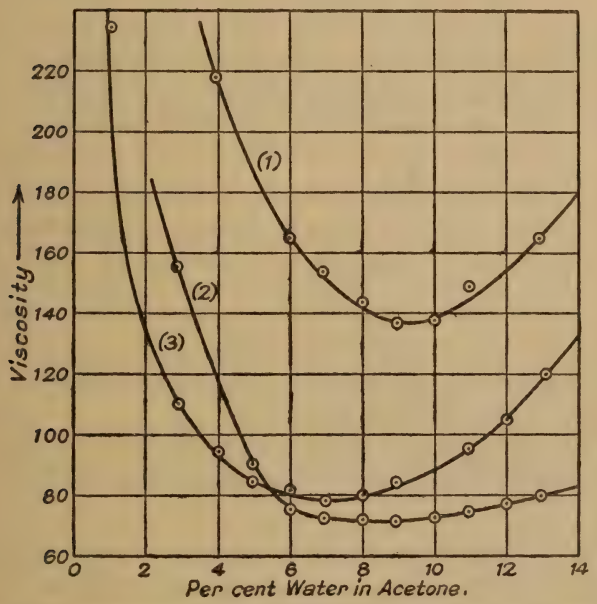


Fig. 4 (Masson and McCall).—These curves show the viscosity of three solutions of nitrocellulose in mixtures of acetone and water, plotted against the composition of the solvent. Note that, in each example, the lowest viscosity is shown, not in anhydrous acetone, but in acetone containing an appreciable quantity of water. The concentration of nitrocellulose is constant along each curve.

Curve 1.—10 grammes of nitrocellulose (12·3% nitrogen) in 100 grammes of solvent.

Curve 2.—8·5 grammes of nitrocellulose (12·3% nitrogen) in 100 grammes of solvent.

Curve 3.—10 grammes of nitrocellulose (13·0% nitrogen) in 100 grammes of solvent.

and that the solvent power of the mixture is due to the complex. Baker rejected the view that the solvent power was due to unassociated alcohol molecules, and that the effect of the ether was merely to increase the number of those molecules, on the following grounds :—

(*a*) It is not true that the higher the degree of association in a homologous series of alcohols, the less is the solvent power. The opposite is the case.

(*b*) If increase in the proportion of unassociated alcohol increases the solvent power, any indifferent liquid added to alcohol should increase the solvent power, but this is not so.

He also attributed the increased solvent power of ether–alcohol at low temperatures [24] to the increase in the proportion of complex at these temperatures.

Gibson and McCall [26] investigated the effect of variations in the proportions of ether–alcohol on the viscosity of solutions of cellulose nitrate, and found that the proportions required to produce the best solvent (*i.e.*, as shown by the lowest viscosity) depended on the nitrogen content of the nitrocellulose, and that the higher the nitrogen content the greater the proportion of ether required in the solvent (Fig. 2).

From the discussion given in the earlier part of this chapter it will be evident that variation in nitrogen content may be, and probably always is, accompanied by independent variation in—

(*a*) the degree of hydrolysis of the cellulose, and therefore in the percentage of hydroxyl groups,

(*b*) the average dimensions, and the range of dimensions, of the nitrated cellulose particles,

(*c*) the percentage of the minor functions of the cellulose, of which only the sulphuric acid ester group need be mentioned here.

Therefore the proportion of ether required to produce the best solvent may be influenced, not only by variation in the nitrogen content, but also by variation in any of these accompanying factors. If, for instance, one sample of cellulose nitrate contains a higher percentage of hydroxyl groups than another, and if we assume that these attract alcohol molecules in preference to ether molecules from the ether–alcohol mixture, we should have a reason why the sample with higher hydroxyl content should require a solvent with a higher proportion of alcohol, and *vice versa*. This conclusion is not inconsistent with Baker's theory that the active solvent is an ether–alcohol complex. Highfield [26] criticises this view on several grounds. In the first place, working with ether–alcohol solutions containing from 10 to 60% of ether, the variation in viscosity is much less when only 2% of water is present than when 7% is present, so that variation in the amount of ether–alcohol complex

is not a predominating factor. Secondly, Gibson and McCall found that a 4% solution of cellulose nitrate containing 11·8% of nitrogen required a solvent of 50% alcohol to yield a solution of minimum viscosity, while if the nitrogen content were 12·5%, the required proportions were 70% ether and 30% alcohol. This implies that an increase of 0·7% in the nitrogen content involves 20% of the alcohol in these 4% solutions, so that in making more concentrated solutions so much alcohol would be used up in saturating the hydroxyl groups of the cellulose nitrate that little would be available for producing the ether–alcohol complex. Therefore it should be difficult to make these more concentrated solutions, which is not the case. Thirdly, if part of the alcohol is required to saturate hydroxyl groups, the composition of the best solvent mixture should vary with the amount of cellulose nitrate to be dissolved, but, in fact, for the same sample, the proportions of ether–alcohol required to give the lowest viscosity are independent of the concentration. Lastly, if solvent power depends on an ether–alcohol complex, one would expect dry ether–alcohol to yield solutions of lower viscosity than those containing water, whereas, in fact, dry ether–alcohol mixed with cellulose nitrate produces stiff jellies which become much more fluid on the addition of a little water.

These objections must be taken into account in constructing any picture of the dissolution of cellulose nitrate by ether–alcohol. It should be pointed out, however, that the suggestion of the selective adsorption of alcohol from ether–alcohol by the hydroxyl groups of dissolved cellulose nitrate forms no part of Baker's theory of a solvent ether–alcohol complex. The influence of the affinity of cellulose nitrate for alcohol molecules, however, cannot be disregarded. Everyone with practical experience of the dehydration of cellulose nitrate with alcohol knows what differences there are between different types of material in the tenacity with which alcohol is retained. Obviously, however, this affinity is only one of several co-existing in equilibrium in an ether–alcohol solution containing water. If one sample of nitrocellulose attracts alcohol molecules more than another, the equilibrium will be displaced in such a direction that a higher proportion of alcohol will be required in the best solvent mixture. This view is *qualitatively* in agreement with the theory of the existence of an ether–alcohol complex, but is quite independent of that theory, and we are far from possessing sufficient data to express the changes in equilibrium quantitatively.

Masson [27] points out that the influence of temperature must

be considered in any general theory. Alcohol or, still better, aqueous alcohol at — 80° will gelatinise cellulose nitrate, whereas ether will not. In an ether–alcohol solution, we do not know how the solvent is distributed between the dispersed cellulose nitrate and the dispersing medium, and we cannot deduce the composition of the phases from the initial composition of the solvent. There is some mutual action between ether and alcohol which favours absorption of these liquids by cellulose nitrate, but at present its nature is undetermined.

A different aspect of ether–alcohol solutions is opened up by

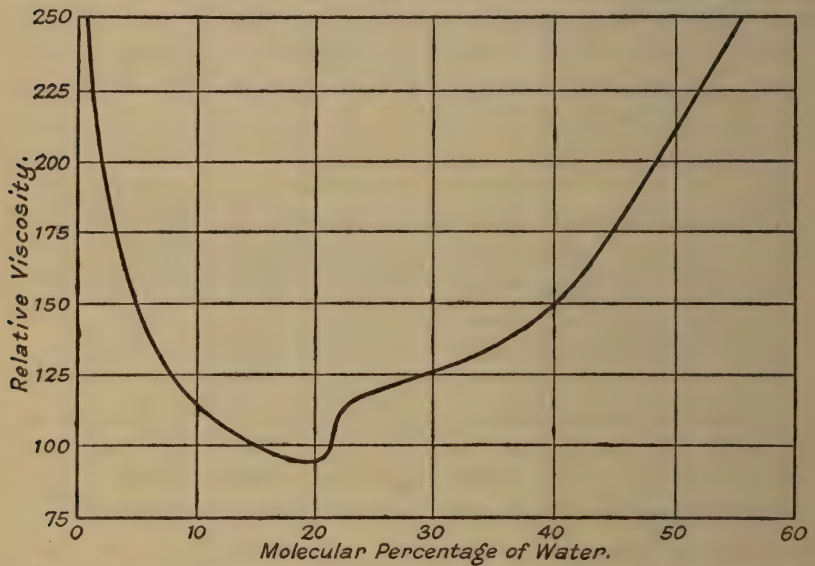


Fig 5. (Barr and Bircumshaw).—This curve shows the viscosity of a sample of Dreyfus cellulose acetate in solvents consisting of various mixtures of acetone and water, the concentration of cellulose acetate being maintained constant at 5%. The viscosities are measured in empirical units and are here only of relative value. Note that the minimum viscosity is shown in a mixture containing about 20 molecules of water %. Compare behaviour of cellulose nitrate in acetone and water, Fig. 4.

Kugelmass,[28] who exposed a sample of cellulose nitrate containing 11·9% to the action of alcohol and ether separately at low temperatures. In each case a sol was formed above the layer of undissolved nitrocellulose. The opalescent ether sol contained nitrocellulose with 13·75% of nitrogen. It was centrifuged until no more solid was deposited, and the cellulose nitrate obtained from it contained 11·20% of nitrogen. The experiment with alcohol carried out in the same way yielded a product with 14·02% of nitrogen. The theoretical di-nitrate requires 11·13%, and the tri-nitrate 14·17%, so that apparently at low temperatures, ether disperses the one and alcohol the other.

Cellulose Acetate in Mixed Solvents.

The solubility relations of cellulose acetate have probably been studied more completely than those of cellulose nitrate. This is due to two causes: (1) the shortage of appropriate solvents during the war, (2) the more restricted range of solubility shown by cellulose acetate as compared with cellulose nitrate.

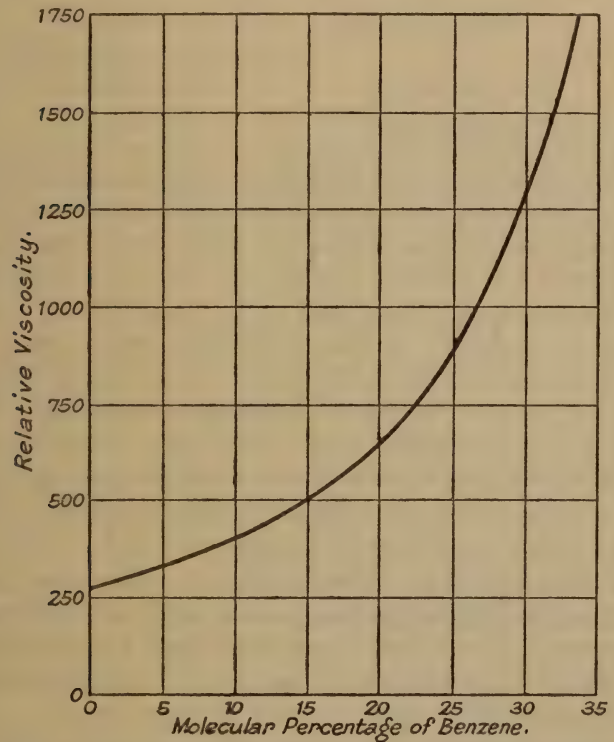


FIG. 6 (Barr and Bircumshaw).—This curve is directly comparable with that shown in Fig. 5, and shows the viscosity of the same sample of cellulose acetate in solvents consisting of various mixtures of acetone and benzene, the concentration of cellulose acetate being maintained constant at 5%. Note that there is no minimum viscosity. Benzene, unlike water, acts throughout merely as a diluent and increases the viscosity of the solution.

Barr and Bircumshaw [29] examined the changes in viscosity of solutions of cellulose acetate in acetone to which varying quantities of water (Fig. 5), alcohol and benzene (Fig. 6) had been added. The concentration of acetate in the solutions was 5%. The addition of alcohol causes a considerable fall in the viscosity, reaching a minimum at about 6% of alcohol and then remaining moderately steady up to a concentration of 40%. Aqueous acetone yielded solutions which had a well-marked minimum viscosity when the

acetone contained 19% (mol.) of water. The addition of benzene to acetate solutions, on the other hand, caused a steady increase in the viscosity of solutions, the curve showing no minimum.

In a number of instances, observers have found minima in the viscosity–concentration curves which approximated closely to a simple molecular combination of the constituents of the mixture, *e.g.*,

1 mol. of tetrachloroethane	+ 1 mol. of alcohol
2 mols. of epichlorohydrin	+ 1 mol. of alcohol
1 mol. of ,,	+ 2 mols. of acetic acid
1 ,, of ethyl formate	+ 1 mol. of acetone
1 ,, of mesityl oxide	+ 1 ,, of alcohol.

Mardles [5] has therefore examined several examples of mixed solvents in which different degrees of affinity would be expected between the constituents. Aniline and acetic acid, for example, form a solvent mixture for cellulose acetate, but also, as a basic and acid compound respectively, react with each other forming compounds which can be isolated. A viscosity–concentration curve for the solvents alone shows a marked peak, *i.e.*, a maximum viscosity at a position close to, but not coinciding exactly with, the point corresponding to a compound of 2 molecules of acetic acid with 1 molecule of aniline. If the same curve is plotted for similar mixtures containing a fixed amount of cellulose acetate in solution, the viscosity maximum is much exaggerated, and is shifted a little nearer to the position of molecular ratios. The curve connecting solvent power number with concentration shows a similar maximum. In this solvent mixture there is no doubt that a complex is formed between the two constituents of the mixture, and that the solvent power is *diminished* by the formation of this complex.

The corresponding curves for a mixture of benzyl alcohol and cyclohexanone show a sag and not a peak, and again the characteristic of the curve is much exaggerated when the mixtures contain cellulose acetate, the sag becoming a V.

The mixture of acetic acid and water shows a well-marked maximum solvent power for cellulose acetate at a concentration of about 36% of water for a 5% solution of cellulose acetate, and the mixture of acetic acid and methyl alcohol a similar maximum at a concentration of about 24% of methyl alcohol. Nevertheless, both of these mixtures show evidence of the formation of a complex between the two ingredients. Hence we have the anomaly that a non-solvent, water, added to a solvent, acetic acid, (*a*) forms a complex with the acid, but (*b*) increases its solvent power. At

first sight this appears to bring us back to Baker's theory of the solvent power being due to the complex, but in view of all the evidence, Mardles concludes that there are instances in which the addition of one liquid to another may result both in complex formation and in molecular simplification (de-association). The increased solvent power is due to the solvent action of the simple molecules produced by de-association of associated molecules. Complex-formation decreases the solvent power, but when complex-formation and de-association occur simultaneously, the favourable influence of the later phenomenon may entirely mask the unfavourable influence of the former.

A few words may be said about other physical properties the study of which has not yet given results comparable with those obtained by studies of viscosity and solvent power in so far as the commercial utilisation of cellulose ester solutions is concerned, but which will have to be considered in any general theory of their constitution.

Viscosity and Plastic Flow.

The experimental and mathematical investigations of Bingham in the United States have stimulated research on the properties actually concerned in viscosity measurements of colloids. It follows from the equation given on p. 60 that if the same liquid is used in the same capillary tube,

$$p = kI,$$

i.e., the curve connecting pressure with outflow is a straight line passing through the point of origin. Bingham and his collaborators have investigated a large number of colloidal solutions in viscometers permitting variation of pressure, and have found that the p/I curve at low pressures is not linear. At higher pressures it becomes linear, and the straight line if produced cuts the pressure axis at a small positive value, *i.e.*, the linear part of the curve is represented by a modified equation $(P - p) = k\,I$, where P is the total pressure applied, and p, the intercept on the pressure axis, is a fraction of the total pressure, which is used up, according to Bingham, in overcoming an internal friction or resistance to viscous flow. This behaviour distinguishes such solutions from pure liquids. Solutions of cellulose nitrate in acetone were studied by Bingham and Hyden,[30] and were found to exhibit the property just described. At temperatures from 5° to 40° the isotherms connecting pressure and outflow are straight lines which by extrapolation cut the pressure axis at points representing small positive values. These small pressures, which must be applied before viscous flow begins, are

termed the yield values. The yield value is not the same for solutions of different concentration, and varies with the temperature. If, however, yield value is plotted against temperature, the curve is again a straight line, which when produced cuts the temperature

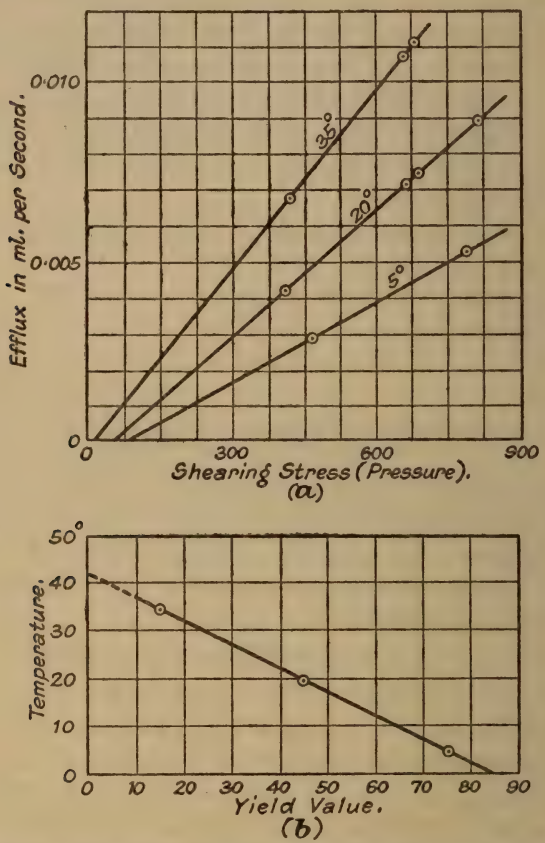


FIG. 7 (Bingham and Hyden).—Graph (*a*) shows the relation between the shearing stress (pressure) and rate of flow through a capillary tube, of a dispersion of a certain sample of nitrocellulose in acetone. Concentration 7·708%. Temperatures 5°, 20°, 35°. The intercept on the pressure axis is friction or yield value *f*, which Bingham defines as the shearing stress at the wall of the capillary necessary to start the flow. Shearing stress is measured in dynes per square centimetre, and efflux in millilitres per second. Note that as the temperature rises, the yield value diminishes. Graph (*b*) shows the yield value of the same solution plotted against the temperature. Note that the curve is linear, and on extrapolation cuts the temperature axis at about 43°. This behaviour suggests that this particular solution becomes a true liquid at 43°, since it is one characteristic of pure liquids that they are deformed by any finite pressure, however small. At lower temperatures the flow of the dispersion is partly a " plastic flow," characteristic of plastic solids.

axis at a point which indicates the temperature at which yield value should be zero, *i.e.*, at which the solution begins to behave like a true liquid (see Fig. 7). It was not definitely settled whether this temperature depends on the concentration.

These observations are of the greatest interest to all chemists working with solutions of cellulose esters, and it is greatly to be desired that they may be continued and extended.

It is impossible in a paragraph to do justice to Bingham's work, and the reader is referred to the bibliography at the end of the chapter for fuller accounts. His view that viscosities of colloid solutions as usually measured are not true viscosities does not invalidate the technical applications of such measurements under fixed conditions in the examination of cellulose esters, but he has already done much to distinguish and define the properties which give these solutions their special qualities, and his work may lead to a more rigid and scientific system for the definition and classification of viscous colloids in general. Bingham's interpretation of viscosity investigations has been vigorously criticised, *e.g.*, by de Waele,[29a] who traverses the physical conceptions which Bingham has developed, and adduces interesting experimental evidence on the flow of petroleum jelly in tubes under low pressure. He also finds departure from linearity in pressure/outflow curves at greater ranges of pressure, and derives an empirical equation

$$p = k\, I^{\phi}$$

connecting pressure and outflow, ϕ being a constant less than unity. Bingham's and Green's reply to the criticism (*ibid.*) should also be read. It seems to the writer that since de Waele's experiments show a marked difference in adhesion between the colloid and the wall of the capillary according to the pressure applied, a complete investigation of the process must take account of the distribution of pressure in a semi-solid, which cannot take the same simple form as in a liquid.

Tyndall Effect.

A beam of light passing through an air space completely free from dust is invisible when looked at in a direction at right angles to the direction of the beam. The same is true of pure liquids when completely free from dust ("optically empty"). Liquids which contain particles in suspension, however, show the path of the light, even in many instances in which the particles are so small or so near in refractive index to the medium that the liquid appears transparent to the naked eye. This property is known from its chief investigator as the Tyndall effect, and has been applied largely to the study of colloidal solutions, particularly in ultramicroscopy. Solutions of cellulose esters show usually a weak Tyndall effect, because the swollen particles have a refractive index very near to that of the medium in which they are suspended.

Mardles[31] examined the variation of Tyndall effect with concentration, using solutions of cellulose acetate, and made the interesting discovery that as the concentration of cellulose acetate increases, the effect rises to a maximum and then falls off (see Fig. 8). For example, solutions of a certain cellulose acetate in benzyl alcohol gave a marked maximum effect at a concentration of 6%. The peak to the curve is much less marked at higher temperatures than at low. The physical significance of this is uncertain. Since the effect is due to the difference between the refractive index of the particles and that of the solvent, when the effect increases there must be either an increase in the difference of

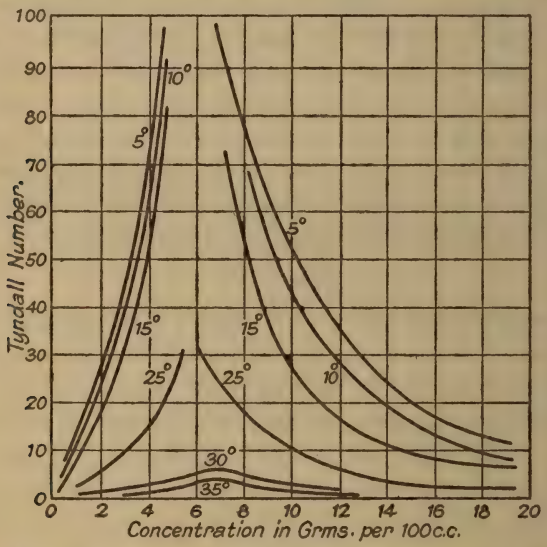


FIG. 8 (Mardles).—These curves show the change of Tyndall number with concentration for a sample of cellulose acetate in benzyl alcohol. Note that there is a very marked maximum at about 6% concentration, but this maximum is much less marked with rise of temperature. At 35° it has almost disappeared. The Tyndall numbers in which the scattering of light is measured are multiples of an arbitrary unit representing the scattering of light by a certain sample of castor oil used as a standard. The comparison was made photometrically.

refractive index or an increase in the amount of surface bounding the two phases, or both. The first condition would be brought about if the additions of cellulose acetate were taken up mainly by particles already existing; the second, either by the change in size or shape of the existing particles, or by formation of additional particles of swollen ester, or by subdivision of existing particles. The latter is so unlikely that it may be left out of account. If we assume the simplest behaviour of all, namely, that the cellulose acetate when dissolved in benzyl alcohol disperses into spheres of uniform size, the maximum surface will be exposed

just before the boundaries of the spheres begin to touch, *i.e.*, when the spheres occupy 71% of the total volume of the solution. If more cellulose acetate is added, the boundaries will begin to coalesce, and the scattering of light to diminish. An explanation on these lines involves the assumption that in a 6% solution of cellulose acetate in benzyl alcohol the swollen particles occupy 71% of the total volume. A paper by Hatschek and Humphry[32] on agar sols and gels should be read in relation to this subject. It was pointed out by Porter in the discussion on the paper that the scattering of light need not indicate any great difference in composition between the two phases, since it varies with the square of the relative refractive index. Hatschek agreed, but said that, on the other hand, it might require a considerable difference in composition between the two phases to cause even a slight alteration in the refractive index.

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CHAPTER VI

CELLULOSE ESTER SOLUTIONS: SOME PROPERTIES. PART II

Swelling—Researches of Knoevenagel and his collaborators—Distribution of Solvent between Swollen Ester and Liquid—Volume Change on Dissolution—Dielectric Capacity—Discussion of Evidence on Constitution of Cellulose Ester Solutions.

Swelling.

Before cellulose esters disperse to form what are usually termed solutions, they undergo swelling, evidently by absorption of one or more constituents of the solvent. They also undergo swelling in some liquids in which they do not disperse. This behaviour was investigated by the late E. Knoevenagel and his collaborators in a series of papers which probably rank with those of Mardles as being the most important of recent contributions to the study of the chemistry and physics of cellulose esters.

The material employed was in all cases cellulose acetate in the form of threads resembling horse-hair. The most interesting experiments were those in which weighed quantities of this material were treated with different combinations of liquids, and the distribution of the ingredients between the swollen ester and the supernatant liquid determined by analytical methods, in many instances specially devised. The results obtained can only be indicated very briefly here, and should be consulted in the original papers, which are worth republishing separately with the correction of some misprints.

Cellulose acetate does not swell either in water or in absolute alcohol, but in mixtures of the two it swells considerably.[1] The degree of swelling is determined by the composition of the mixture, and exhibits a maximum. It is not changed if, after equilibrium is reached, the organic portion of the solvent is entirely displaced by water. Swollen cellulose acetate is dyed by methylene-blue, or saponified by alkali, much more readily than the unswollen material, and these two processes run parallel with each other and with the degree of swelling.

When cellulose acetate [2] is shaken with different aqueous solutions of aniline, phenol or ethyl tartrate, these ingredients are found after 24 hours to be distributed between the ester and the water according to the Distribution Law :—

$$C_A = kC_S$$

where C_A = the concentration of, say, aniline in the swollen acetate, C_S = concentration of aniline in the liquid layer, and k = constant. This Law of Distribution is usually applicable to the equilibrium between two immiscible *solutions* of a common solute (*e.g.*, to the

partition of picric acid between benzene and water in contact). Hence these experiments make it probable that when cellulose acetate swells, it takes up molecules as if it were a solvent of them, and not by adsorption at the surface.

Measurements were next made [3] of swelling in the binary mixtures benzene–alcohol, nitrobenzene–alcohol, carbon tetrachloride–alcohol. If the pure liquids were employed, the order of swelling, in decreasing values, was nitrobenzene, benzene, alcohol and carbon tetrachloride, of which only nitrobenzene could be called a powerful swelling agent. The surface tensions of these pure liquids decrease in the following order—nitrobenzene, benzene, carbon tetrachloride, alcohol. In binary mixtures, alcohol always caused a lowering of surface tension, and a qualitative relation was found between the degree of swelling and the lowering of surface tension. The greater the reduction of surface tension caused by the addition of alcohol, the greater the swelling action of the mixture. Since, however, alcohol alone has no swelling action on cellulose acetate, a maximum of swelling effect is reached at a certain concentration.

A relation was then sought [4] between the degree of swelling (which precedes dispersion) and the viscosity of the solutions after dispersion. The viscosity–concentration curves were plotted for various mixtures of ethyl alcohol and nitrobenzene, and it was found that the viscosity curve for a liquid of weaker swelling power always lies below that for a liquid of stronger swelling power. An interesting regularity observed was that for any two mixtures of alcohol and nitrobenzene, the ratio of the viscosities at equal concentrations of cellulose acetate was constant. It was also found that the concentration–viscosity data for any one solvent mixture were approximately fitted by the equation

$$\text{concentration} = \text{constant} \times \text{log. of viscosity.}$$

(The statement in the original paper, *Koll. Chem. Beihefte*, 1921, **13**, 267, " Die Viskosität steigt im gleichen binären Lösungsgemisch bei zunehmenden Azetylzellulosegehalt annähernd proportional mit den Logarithmen der inneren Reibung an," is an evident slip.)

Further investigations into the system cellulose acetate–nitrobenzene–alcohol [5] confirmed previous work by showing that the nitrobenzene over a range of concentrations obeyed the Distribution Law (Henry's Law), *i.e.*, there was a constant ratio between the concentration of nitrobenzene in the liquid and in the swollen solid. It was also found that alcohol was taken up in constant amount by the cellulose acetate through a considerable range of mixtures

containing small concentrations of nitrobenzene. The experiments were extended [6] to the mixtures acetic acid–water, acetic acid–benzene, acetone–benzene, nitrobenzene–isopropyl alcohol, ethyl alcohol–benzene, nitrobenzene–benzene, ethyl alcohol–water, acetic acid–nitrobenzene, acetone–nitrobenzene, methyl alcohol–nitrobenzene, acetone–methyl alcohol, acetic acid–camphor. It now begins to be difficult to follow the deductions which Knoevenagel made from the experimental results. Consider, for example, the system cellulose acetate–benzene–acetone. It is stated that there is a constant ratio of cellulose acetate to benzene in the swollen acetate; also that both benzene and acetone are distributed between the liquid and the swollen acetate according to Henry's Law. Using his nomenclature, we have :—

In the liquid $\begin{cases}\text{mols. of acetone per cent.} = a.\\ \text{mols. of benzene per cent.} = b.\end{cases}$

In the swollen acetate $\begin{cases}\text{mols. of acetone per cent.} = c.\\ \text{mols. of benzene per cent.} = d.\\ \text{mols. of cellulose acetate per cent.} = e.\end{cases}$

(assuming a C_6 unit of cellulose acetate).

It is stated (p. 186) that $\frac{a}{c}$ = constant (mean value 1·05, range 0·91 to 1·18).

$\frac{b}{d}$ = ,, (mean value 1·11, range 0·85 to 1·26).

$\frac{d}{e}$ = ,, (mean value 5·09, range 4·31 to 7·42).

If these three relations are all true, it follows that

$$\frac{b}{e} = \text{constant}.$$

Actually $\frac{b}{e}$ varies from 8·8 to 1·7, so that it appears that the constancy of one or more of the three ratios mentioned above has been too readily assumed. It is greatly to be desired that this matter should be cleared up, preferably by some of Knoevenagel's collaborators, as the experimental work forming the basis of this series of researches is invaluable. It is right to add that Knoevenagel admitted the existence of deviations in this series, probably owing to the chemical relations between acetone and benzene, and the solubility of cellulose acetate in acetone.

His general conclusion is that alcohol, benzene and water are taken up in constant quantities from various mixtures, and this

suggests that swelling is due to chemical action and not to surface adsorption. The affinities concerned are probably of a different order from those concerned in typical molecular compounds.

In the next paper,[7] similar experiments are described, from which it is concluded that from binary mixtures of alcohol, nitrobenzene and benzene, liquid is absorbed by cellulose acetate in molecular proportions. The sum of the number of molecules of each liquid taken up from a binary mixture by cellulose acetate is constant. Determinations of heat change support the view that swelling is a molecular process.

In the last publication,[8] it is shown that cellulose acetate which has been brought into equilibrium with a solvent in which it swells considerably, will, if placed in a solvent with smaller swelling power, shrink until it possesses the same degree of swelling as it would have had if it had been placed originally in the second solvent. This is in contrast with the behaviour noticed with water, which can entirely replace an aqueous–organic swelling mixture such as alcohol and water, without changing the degree of swelling. Probably the water, which has no swelling action whatever, hardens the original swollen structure and sets it.

Volume Change on Dissolution.

Mardles [9] found that when cellulose acetate is dispersed in a solvent, a slight contraction in volume takes place. With simple solvents, the greatest contraction takes place with the best solvents. With mixed solvents, the contraction is greatest with the mixture of highest solvent power. It is proportionately greater at low concentrations and at high temperatures, *i.e.*, under those conditions in which the dispersion approaches most closely to a molecular solution.

It should be noted that these observations refer to the system as a whole, whereas the " swelling " studied by Knoevenagel and his collaborators refers only to the colloid. Thus the colloid swells (by absorption of solvent molecules), but the system as a whole contracts. Further, Knoevenagel found that solvent mixtures in which the swelling was small yielded solutions of lower viscosity than those in which swelling was great. It is generally agreed now that solutions of low viscosity indicate high solvent power, and it would be expected that when the swelling of the colloid was least, the contraction of the whole system would be greatest. Hence we see a qualitative connection between low swelling of the colloid, high contraction of the system, and low viscosity of the solution.

Dielectric Capacity.

Fenton and Berry [10] thought from the investigation of the solvent power of a large number of simple liquids for cellulose acetate that there was some relation between the dielectric constant and solvent action, although there were admittedly exceptions. Mardles [11] quotes a number of these exceptions and points out that the dielectric constant diminishes with rise of temperature, whereas solvent action increases.

Conclusion.

The preceding discussion on some of the properties of solutions of cellulose esters which are most nearly related to their industrial application, furnishes material for provisional views of their nature.

The dispersion of a cellulose ester by a simple or mixed solvent obviously depends in some way on the attraction exerted by the molecules of the solvent, or some groups in the molecules, on some of the distinctive groups in the esterified cellulose. Nevertheless, it must always be remembered that any picture based on this consideration alone will be incomplete, since on this view cellulose, with its high percentage of hydroxyl groups, should be soluble in water. The secondary affinities, which bind together the C_{18} units of cellulose proposed by Irvine, still exist in the cellulose ester, although probably they are weakened.

Esselen [12] was apparently the first to suggest the application of Langmuir's theory of film adsorption to the dispersion of cellulose esters. Considering the example of cellulose acetate dispersing in certain mixtures of chloroform and alcohol, he assumes that the surface of cellulose acetate attracts the hydroxyl groups of the alcohol and adsorbs the alcohol in such a way as to hold the hydroxyl groups next to the acetate, leaving the hydrocarbon (ethyl) radical projecting into the solution. These hydrocarbon groups may attract the hydrocarbon end of the chloroform molecules. Both of these processes would induce swelling and tend to disperse the cellulose acetate. Esselen further suggests that the composition of the best solvent mixture may coincide with the point at which all the secondary valencies at the surface of the acetate are just saturated by the alcohol. With technical cellulose acetate this point corresponds with 25 to 30% alcohol in the solvent.

As a second example, Esselen considers the solubility of some varieties of cellulose acetate in a warm mixture of alcohol and benzene, although they are soluble in neither constituent alone nor in the mixture when cold. In this instance he supposes a similar

adsorption of alcohol by the ester, and an attraction between the ethyl radical of the alcohol and the benzene hydrocarbon. That a paraffin hydrocarbon does not behave similarly he explains by the known fact that the paraffin hydrocarbons and alcohol are only very slightly miscible, so that if the ester only dissolves in the alcohol–benzene mixture with difficulty, one would not expect the alcohol–paraffin mixture to possess any solvent power at all.

Esselen then extends the theory to compounds possessing the aromatic nucleus and the hydroxyl group in one molecule and suggests that this may explain the high solvent power of the phenols. [Perhaps a better example still would be benzyl alcohol.]

This theory appears to contain the germ of a rational mode of viewing the dispersion of cellulose esters, and it is worth examining in the light of the evidence summarised in previous pages. If the best solvent mixture corresponds to a point at which the surface is entirely saturated with alcohol, the composition of the best solvent mixture should vary with the concentration of the ester. On this point there is conflict of evidence. Highfield states that, in the instance of cellulose nitrate and ether–alcohol, the composition of the best mixture is independent of the concentration, while Masson and McCall, working with acetone and water, found slight variations with the concentration. It does not seem to be necessary to assume that the whole of the alcohol in the best solvent mixture is adsorbed at the surface of the ester and it is not clear that this is Esselen's assumption. It is more reasonable to assume an equilibrium between the alcohol so adsorbed and the alcohol in the surrounding medium. A change in the concentration of the ester would displace this equilibrium, but would not lead to a quantitative adsorption of more ethyl alcohol exactly proportionate to the fresh surface of ester supplied. Another factor which may enter here is that the swelling of the ester may itself open up fresh surface to the adsorption of alcohol, and if this is inhibited in any way at higher concentrations, the amount of surface will not be proportional to the concentration.

The dispersion of the ester would therefore be due to the affinity of one or more constituents of the solvent mixture for groups on the surface of the particle of cellulose ester, some of these groups being formed by the particle selectively adsorbing constituents from the solvent mixture itself. Hence, in a restricted sense, the formation of a complex between the constituents of a binary mixture may be related to its solvent power, provided that one constituent of the complex is also selectively adsorbed by the particles of cellulose ester. This constituent acts as a link between the cellulose ester

and the solvent medium, and through it the molecular motion of the latter is transmitted to the ester as a dispersive influence. Since vapour pressure is a manifestation of molecular energy, we see why substances of low boiling point are more active constituents of solvent mixtures than their homologues of higher boiling point, and it is interesting that chloroform and ether, which when mixed with alcohol form solvents for cellulose acetate and nitrate respectively, are both liquids of high vapour pressure. Possibly this property is also a factor in the use of the volatile substance carbon di-sulphide in the viscose reaction.

Single solvents must be regarded as combining in one substance the function of being adsorbed by the cellulose ester, and of being attracted also by the molecules of their own kind in the remainder of the solvent medium. Thus, the solvent action of benzyl alcohol on cellulose acetate would be explained by the selective adsorption of the hydroxyl group by the particles of cellulose acetate, and the attraction between the remainder of the molecule, namely, $C_6H_5 \cdot CH_2 \cdot$, and the rest of the benzyl alcohol in the solvent. Such an attraction would be expected to manifest itself in a certain degree of association in the pure solvent, and we have a speculative explanation of the fact that associated liquids are frequently good solvents.

The increased solvent power frequently imparted by small quantities of water in solvents may be due to a similar attraction between hydroxyl groups in the ester and water molecules, and the complex so formed may then adsorb some water-soluble constituent of the rest of the solvent. Worden [13] states that if the acid hydrolysis of cellulose acetate is unduly prolonged, the resulting product will take more and more water in its solution in acetone without precipitation. There is an undoubted relation between these factors, and also a possibility that the ester groups themselves may have an inherent attraction for water molecules, since all the inorganic nitrates are soluble in water, and most of the acetates.

It is not profitable, however, in the present state of our knowledge to push the theory of selective solvent absorption or adsorption too far. There are specific influences at work also, which must explain why alcohol and chloroform disperse cellulose acetate and not cellulose nitrate, while ether and alcohol disperse cellulose nitrate and not cellulose acetate; in each case we certainly have adsorption of alcohol and some affinity between the alcohol and the other ingredient; yet entirely different behaviour. Perhaps the underlying attraction of the theory of selective absorption is that it

suggests an analogy with selective permeability of membranes, and a possibility of applying a modification of Donnan's theory of membrane equilibria to the swelling of cellulose esters, thus bringing them into line with gelatin.

Against the suggestion that the dispersion of cellulose esters in a solvent may be brought about by selective adsorption of constituent groups of the solvent mixture *at the surface* of the ester particles, must also be placed the weight of evidence adduced by Knoevenagel. If solvent molecules are absorbed by the ester so that the ratio of the number of molecules to the number of C_6 units is constant, Knoevenagel appears to be justified in assuming the formation of some kind of molecular compound, and in asking the question—What has become of the surface? Perhaps, after all, this is only a restatement of an old difficulty. What structure is it that prevents cellulose dissolving in water and yet allows the penetration of a nitrating acid mixture (presumably) to every C_6 unit in the mass? A great deal more experimental evidence is required, particularly along the lines indicated by Knoevenagel, before these questions can be answered.

In regard to the molecular dimensions of the particles in dispersions of cellulose esters, there is also contradictory evidence. Böeseken and his collaborators think that there is not a great range of dimensions, *i.e.*, that n does not vary much in the particles of cellulose acetate when acetylation and the accompanying hydrolysis are not pushed too far. Duclaux and Wollman, on the other hand, find a wide range of viscosities in the products of the fractional precipitation of cellulose nitrate, and the same fact holds for cellulose acetate. Since nitration is a shorter process than acetylation, one would expect the range of dimensions of cellulose nitrate to be at any rate no greater than that of cellulose acetate. One way of reconciling the two views is to assume that a comparatively small difference in the average value of n causes a large difference in the viscosity of the solutions.

The peak in the curve connecting Tyndall effect and concentration (Mardles) requires much more investigation, using different esters and different solvents. Since the cellulose esters usually differ in refractive index from their solvents, a dispersion of the ester in the solvent would be expected to show a Tyndall cone, as long as the particles were not too small. If, however, the particles swell very considerably by adsorption of solvent, the difference in refraction between the two phases must diminish and the Tyndall cone become less marked, unless we assume that orientated benzyl

alcohol molecules, *i.e.*, as produced by a shell of $C_6H_5 \cdot CH_2 \cdot$ groups forming the outside of a cellulose acetate particle which has selectively adsorbed the ·OH groups, have a different refractive index from normal benzyl alcohol. It has already been suggested that the peak may represent the maximum development of surface before envelopes of solvent, surrounding ester particles, begin to coalesce. If so, there should be a relation between this curve and the curve connecting concentration with yield value (Bingham). An investigation on these lines would be more likely to yield results of value if the particles were of approximately uniform size, and this condition could be partly realised by using the products of a fractional precipitation (Duclaux) as working material. Further, Mardles found that the peak diminished and disappeared with rise of temperature, while Bingham (with a different ester and solvent) found that solutions showing zero fluidity approached and finally attained the status of true liquids with rise of temperature. A relation should be sought between these phenomena, to see whether the temperature at which a cellulose ester dispersion becomes a true solution is coincident with, or related to, the temperature at which the peak in the Tyndall–concentration curve disappears.

This short survey of recent researches on the properties of cellulose ester solutions is enough to show that much remains to be done, and a great deal of the work can best be carried out in academic research laboratories. Many of the measurements required, though comparatively simple and involving no great manipulative skill, are tedious and require for their performance a degree of freedom from the claims of other interests which can seldom be realised in a factory laboratory. Apart from their scientific interest, there is always the possibility of discovering some fact of immediate technical value.

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CHAPTER VII

INGREDIENTS OF CELLULOSE ESTER VARNISHES

Inflammability of Solvents—Inflammability of Coatings—Choice of Solvents and Diluents—Application of Laboratory Results—Variation in the Esters—Commercial Solvents of Esters—Approximate Classification—Specifications for Acetone, Methyl Ethyl Ketone, Methyl Acetone, Ethyl Alcohol, Methyl Alcohol and Wood Spirit, Ether, Ethyl Acetate, Butyl Acetate, Amyl Acetate, Ethyl Lactate, Acetone Oil, Diacetone Alcohol, Tetrachloroethane, Benzene, Toluene, Butyl Alcohol, Amyl Alcohol, Triacetin, Benzyl Alcohol, Triphenyl Phosphate, Castor Oil—Resins—Shellac, Mastic, Copal, Sandarac, Dammar—Typical Resin Formulæ.

The processes and considerations involved in the manufacture and application of cellulose nitrate and cellulose acetate varnishes are so similar that it is best to treat them together. The choice between the two is mainly that of price, but occasionally other considerations occur, such as the inflammability of the coating or the resistance of the coating to particular solvents.

In regard to inflammability, misapprehensions have frequently arisen as to the comparative dangers of the two esters. Dry cellulose acetate itself, the base of the acetate varnishes, is usually termed non-inflammable—generally as a distinction from cellulose nitrate—because although it will burn (*i.e.*, is combustible), it burns quietly and presents no special fire danger. Dry cellulose nitrate, on the other hand, burns fiercely, and in the higher nitrations is explosive under certain conditions. The solutions of these esters which are employed as varnishes, however, invariably contain volatile inflammable solvents or diluents such as acetone, methyl alcohol, ethyl alcohol, benzene and ethyl acetate, to which they owe their property of drying quickly. The danger incurred in the *application* of these varnishes is therefore practically equal for both esters, since it arises only from the accumulation of inflammable vapours in the working rooms, unless simple precautions are taken in regard to ventilation. These inflammable vapours in certain ranges of concentration form explosive mixtures with air, and even when all precautions are taken, naked lights, fires or smoking should never be allowed in the work-rooms. Exactly the same precautions are necessary with the so-called spirit varnishes, which consist chiefly of resins dissolved in methylated spirit. The danger during application has nothing to do with the solid materials dissolved in the solvents; it arises from the properties of the solvents alone.

When the volatile solvents have dried out, leaving the film of cellulose ester, with or without softeners, resins or pigments, a new set of conditions arises. The film of cellulose nitrate, taken alone and away from any support, is still highly inflammable. If, however,

the film is attached to a support—as in practice it always is—the danger due to its inflammability in most cases disappears. On a metal surface, the film cannot be made to ignite, as the application of a flame only causes it to blister and decompose without flaming. Wood coated with the varnish is no more easy to ignite than uncoated wood. In fact, one may say that in general the fire danger of materials coated with a cellulose nitrate varnish is the same as that of the materials alone.

There is, however, one important class of exceptions—that of textiles covered with a thick protective coating of cellulose ester. In this instance we have an inflammable fabric, together with a coating which forms an appreciable fraction of the total weight of the coated material. Here a cellulose nitrate coating is an added danger, and it is from this fact that the use of cellulose acetate varnishes for aeroplane fabrics has become so extensive. Even cellulose acetate varnishes for this purpose often have special ingredients added so as to reduce their non-inflammability to incombustibility, since the film from a varnish not so treated is usually appreciably more inflammable than the original cellulose acetate base, on account of the inflammable organic softeners and solvents of high boiling point which it contains.

Choice of Solvents.

In nearly all technical varnishes based on cellulose esters, the solvent is a mixture of several liquids. The reason for this is obvious. The chief advantage possessed by these varnishes over oil varnishes is their rapid rate of drying, due to the volatility of their solvents. If, however, a varnish is made up entirely from a solvent of low volatility, *e.g.*, acetone, it is found that the rapid rate of drying entails such a marked fall in temperature at the surface of the film that the atmosphere begins to deposit moisture upon it, causing precipitation of the ester and sometimes pitting of the film. This tendency imposes a practical limit on the rapidity of drying which can be allowed in a commercial varnish and will be considered in more detail in a later section.

The varnish must therefore contain only a limited quantity of highly volatile solvents if it is to dry in a normal atmosphere with a bright surface and a coherent structure. To lower the rate of evaporation we must add a solvent of higher boiling point, and quite satisfactory varnishes for many purposes can be made from a simple mixture of solvents with boiling points varying from low (*e.g.*, about 50°) to high (about 130°). Here, however, considerations of cost

enter. Solvents of the cellulose esters are usually comparatively expensive materials, and we have to find in what way we may dilute these expensive ingredients with cheaper materials without interfering with their properties as varnishes. These diluents must, of course, be miscible with the solvents used. They must not precipitate the cellulose ester from the solution, and this condition must hold not only in the original varnish, but at all stages of the evaporation of the volatile ingredients. For example, a solution of cellulose nitrate in acetone could easily be diluted with a considerable quantity of xylene without precipitating the ester. If, however, such a solution were poured on to a glass plate and allowed to evaporate, even in a perfectly dry atmosphere so that no deposition of moisture was to be feared, it would not form a satisfactory film. The acetone would evaporate much more rapidly than the xylene, and the point would soon be reached at which the cellulose nitrate would begin to separate from the solution. The final product would be an opaque, flaky and brittle deposit of no value.

If, however, a diluent is chosen having a suitable rate of evaporation, it is possible to make use of it. For example, a solution of cellulose nitrate in amyl acetate may be considerably diluted with a light petroleum spirit, *e.g.*, one which distils between 50° and 120°, without precipitating the ester, and during the evaporation the amyl acetate may be continuously present in sufficient quantity to keep the ester in solution. Under these circumstances a clear tough film is formed.

The preceding chapters have shown, however, that there are other cheap diluents which may be used in combinations which actually assist the true solvents. Thus alcohol has been shown to reduce the viscosity of solutions of both cellulose acetate and cellulose nitrate, when used in certain combinations. For example, alcohol and toluene together have a solvent action on some grades of cellulose nitrate, and alcohol and benzene a weaker solvent action on cellulose acetate, and it is for this reason that the laboratory researches on the solvent power of these mixed liquids are so important. Since alcohol and the coal tar distillates are cheaper than most of the true solvents, the use of certain combinations of them as diluents of the true solvents will often achieve considerable economy without detriment to the varnish.

Application of Laboratory Results.

These combinations must, of course, be chosen with considerable care, and much experience is necessary in applying the results of laboratory work to technical manufacture. Apart from the

necessity of avoiding excessively rapid evaporation and the precipitation of the ester at any stage of evaporation, three other considerations enter :—

(1) Most laboratory investigations are rightly carried out with chemically pure solvents. Technical solvents are seldom chemically pure and in some cases the degree of impurity may be somewhat large. The influence of these impurities is irregular. Often it may be favourable, as in the presence of traces of acetone in methyl alcohol (as a cellulose nitrate solvent), or of acetone in methyl ethyl ketone (as a cellulose acetate solvent). Whether favourable or unfavourable, however, the presence of these impurities complicates the direct application of the results of research.

(2) When a solvent contains three or more ingredients (and in practice simpler mixtures are rare) the application of the results of the investigation of binary mixtures becomes very complicated, even if the ingredients are chemically pure. Take for instance a mixture of amyl acetate, ethyl alcohol, benzene and acetone. It could be regarded as a mixture of two binary mixtures, (1) amyl acetate + ethyl alcohol, (2) benzene + acetone, and the solvent properties of these separate mixtures might be known, but it would be impossible to forecast the solvent properties of the complete mixture by making use of this knowledge alone. Each one of these ingredients gives characteristic viscosity and solvent power curves with each of the other three, and the mutual interaction of all these manifestations of affinity cannot be accurately gauged.

(3) A point which is repeatedly overlooked in patent and other literature is that no two samples of cellulose ester can be guaranteed to be exactly alike. Profound differences are possible in solubility, in viscosity and in chemical composition. Even with the most careful control of manufacture small variations occur in cellulose esters made by the same process and in the same factory, and between one manufacturer's product and another there may be considerable differences due to variations in the raw material, composition of the esterifying mixture and the time and temperature of esterification.

It follows from the last paragraph that the value of long lists of formulæ of cellulose ester varnishes is doubtful, especially since the advent of cellulose nitrates of unusually low viscosity. For instance, two separate samples of cellulose nitrate varnish might

be made up to exactly the same formula. One might yield a stiff jelly which would not flow appreciably when the vessel containing it was inverted. The other might give a solution more fluid than glycerine. The chief interest and value of published formulæ lie in the manner of combination of the solvents.

In a recent circular, Gardner and Parkes[1] discuss the rate of evaporation of solvents from pyroxylin lacquers, on the whole along well-known lines; there are, however, some points of interest. Too rapid evaporation of the solvent causes the faults variously described as pin-holing, goose-fleshing and the orange-peel effect. Tests on the rate of evaporation of individual solvents alone, at ordinary temperatures, show that the order in which the solvents are placed by this test does not exactly coincide with the order of the boiling points; for example, ethyl alcohol evaporates into the air more slowly than ethyl acetate, although the boiling points are almost identical. This was to be expected, since the rate of evaporation at ordinary temperatures depends on the vapour pressure at that temperature, and the vapour pressure curves of different substance may cross one another; the boiling point is only a rough, but nevertheless useful, indication of the rate of evaporation at ordinary temperatures. Curves are given for the rate of drying of solutions of nitrocellulose in ethyl acetate, denatured alcohol (using a special alcohol-soluble nitrocellulose), diethyl carbonate, butyl acetate and amyl acetate. The time taken for 87% of the solvent to evaporate is given in the following table :—

Ethyl acetate	30 mins.
Ethyl alcohol	77 ,,
Diethyl carbonate Butyl acetate	110 ,,
Amyl acetate	170 ,,

The test with ethyl alcohol is hardly comparable with the others, since it was carried out with a special nitrocellulose, and the nature of the dissolved ester undoubtedly influences the rate of evaporation. The other four tests were carried out with the same sample of nitrocellulose.

Curves are also given showing the rate of evaporation of butyl acetate from solutions of different concentration of the same nitrocellulose. These all appear to reach approximately constant weight in 120 minutes on filming, although the amount of solvent left in the films varies from 3% for the thinnest film to 26% for the thickest

film. Closer investigation would, no doubt, show that the thicker films were still losing solvent at a slow rate. The writer's experience in the celluloid industry is that there is a rapid loss of solvent from unseasoned material in the first few hours which is practically the same *per unit of surface* whether the material is thick or thin. The rate quickly diminishes, but thick material will continue to lose weight long after thin material is practically dry.

Commercial Solvents for Cellulose Nitrate.

The principal solvents in use for cellulose nitrate varnishes are acetone, methyl alcohol, ethyl acetate, butyl acetate and amyl acetate. Of these, ethyl acetate is used more in the United States than in this country. Acetone and methyl alcohol are both highly volatile at ordinary temperatures, and solutions in either of these solvents will not give clear films unless special precautions are taken to reduce the humidity of the air and the rate of evaporation. Butyl acetate and amyl acetate are used in nearly all the technical varnishes, as, owing to their low vapour pressure, they retard the rate of evaporation and diminish the tendency of the film to absorb moisture from the atmosphere. They can be used with diluents having a vapour pressure only slightly less than their own, as long as they are present in sufficient amount throughout the evaporation to prevent separation of the cellulose nitrate. According to Wiesel,[2] diethyl carbonate is being introduced as a solvent in the United States. Cyclohexanone and cyclohexanyl acetate have also been suggested, but have not yet come into general use. The chief diluents are ethyl alcohol, benzene, toluene, butyl alcohol and amyl alcohol (or fusel oil). Ethyl alcohol is present in practically all cellulose nitrate varnishes, since it is used to expel water from the original cellulose nitrate in the dehydration process. It is not simply a diluent, since it develops the solvent power of some other solvents. Benzene and toluene are both coal-tar fractions. They have no solvent power of their own, but are partial or complete solvents when mixed with alcohol in certain proportions. When toluene, which has a lower vapour pressure than benzene, is used, special care must be taken that there is sufficient butyl or amyl acetate present to counteract its lack of solvent power when the bulk of the alcohol has evaporated.

Finally, it may occasionally be economical to dilute a solution with an entirely indifferent liquid which has no solvent power, either alone or in combination, at ordinary temperatures. The only liquid of this class used commercially is a light petroleum spirit.

The heavier paraffin distillates are too slow in evaporation, and would not satisfy the condition that the true solvents must be in excess throughout the evaporation.

Cellulose Acetate Solvents.

These may be considered under practically the same headings as cellulose nitrate solvents. Clément and Rivière [3] classify the acetate solvents as follows :—

(1) Direct volatile solvents : Acetone, methyl acetate, methyl and ethyl formates, diacetone–alcohol, nitromethane, formic and acetic acids, pyridine, ethyl acetoacetate, benzyl alcohol, furfurol.

(2) Indirect volatile solvents : Hot alcohol and benzene, chloroform and alcohol, tetrachloroethane and alcohol.

(3) High-boiling gelatinising solvents : Acetins, particularly triacetin, diphenyl ethers of glycerin, glycerin benzoate, glycol–chlorohydrin, resorcin diacetate, eugenol, butyl and amyl tartrates, dimethyl phthalate.

One may say roughly that, in the above list, acetone, methyl acetate and methyl and ethyl formates correspond to the highly volatile solvents used in cellulose nitrate varnishes. To these may be added methyl ethyl ketone, which, although not a solvent when chemically pure,[4] always contains, in its technical form, sufficient acetone to make it one. Benzyl alcohol, eugenol and the acetins are similar in function to butyl and amyl acetates in cellulose nitrate solutions; while alcohol and benzene, alcohol and chloroform, alcohol and tetrachloroethane are binary mixtures possessing definite solvent power and not to be classified as mere diluents. Entirely indifferent diluents such as petroleum spirit do not appear ever to be used in cellulose acetate solutions. The solvents used in the Air Ministry dopes are acetone, methyl ethyl ketone, alcohol, benzene and benzyl alcohol. Many of the additional substances in Clément and Rivière's list were used to a greater or less extent during the war, but have been entirely displaced by cheaper solvents since.

Specifications of Cellulose Nitrate and Acetate Solvents.

Specifications for all of the usual solvents have been published by the British Engineering Standards Association in accordance with the best commercial practice. They are copyright, and can be obtained from the Secretary, 28 Victoria Street, London, S.W.1, at 2*d.* each, post free.

These specifications refer generally to materials required for Air Ministry Dopes, and in most cases it may be advisable to make them more or less stringent for other commercial purposes. On the whole, however, they form a reasonable basis for the examination of solvents.

In general, it may be said that a high standard of chemical purity is not necessary for the ingredients used in the preparation of cellulose ester varnish, since it follows from what has been written before that the solvent power of mixtures is often greater than that of either ingredient singly; but it is clearly necessary for the buyer to know what he is buying, and to have the mixing under his control. Further, there are certain classes of impurities which must be stringently guarded against. One of these is acidity. Both the acetate and the nitrate of cellulose are sensitive to strong acids, and even weak acids such as acetic acid may be harmful in their effects on containers, pigments, or fabrics. A second harmful impurity is water. Although water in small amounts increases the solvent power of some solvents, in large amounts it acts as a precipitant and destroys the tenacity of the coating. It must also be remembered that considerable cooling takes place when a cellulose ester coating is drying, and this always results in a certain amount of moisture being absorbed from the atmosphere, even if the original ingredients were anhydrous. A third undesirable impurity is solid foreign matter, either suspended or dissolved in the solvent. Suspended solids can be removed by filtration, but dissolved solids will be left in the varnish coating.

Hence specifications of cellulose ester solvents usually contain the following clauses: Water content, acidity and residue on evaporation are strictly limited. Other impurities are limited by determinations of one or more physical properties such as specific gravity, range of temperature of distillation, refractive index, miscibility with specified liquids or solutions, and colour. Usually also, if practicable and convenient, there is a chemical determination of the percentage of the pure chemical compound in the sample.

Specifications for Cellulose Nitrate and Cellulose Acetate Solvents.

The following are typical specifications for some of the commoner solvents and diluents used in the cellulose ester varnishes :—

Acetone.—Until the introduction of the new cordite (R.D.B.) during the war, acetone was used principally as a solvent for gun-cotton, and the best quality was supplied to the British Government

Specification (usually abbreviated B.G.S.). This specification is still used almost universally in commerce.

B.G.S. acetone must be colourless and transparent, and must mix with distilled water in any proportions without showing turbidity. It must leave no residue when evaporated to dryness. Its specific gravity at 15°/15° must not exceed 0·800. If 100 c.c. of the acetone is mixed with 1 c.c. of a 0·1% solution of potassium permanganate the colour must not be discharged in less than 30 minutes in the dark at a temperature of 15°. This last test, known as the permanganate test, is the one on which acetone is most frequently rejected. In 1904, as a result of researches by Marshall,[5] a clause was added to the specification to ensure that the acetone should not contain more than 0·002% of carbon dioxide, and should be otherwise quite neutral. Carbon dioxide has no harmful effect in the manufacture of lacquers, and it is usual only to limit the percentage of acidity and basicity (*v. infra*).

A useful additional test is the amount of discoloration on exposure to light. This is important if the acetone is to be used in colourless or delicately tinted lacquers.

The B.E.S.A. specification differs in some particulars from the B.G.S. The limits of specific gravity are given as 0·769 and 0·801 at 15°, and a distillation test is included providing that 95% must distil between 55° and 60° at 760 mm. pressure. Titration tests are included to ensure that the acidity and alkalinity do not exceed 0·01% calculated as acetic acid and as caustic soda respectively. The time in the permanganate test is reduced to 10 minutes, and the amount of acetone in the sample is estimated by a titration method.

Until shortly before the war, acetone was derived entirely from the distillation of wood, and the separation of pure acetone from the crude distillate, containing water, methyl alcohol, acetic acid, various other ketones and pyroligneous impurities, is technically difficult. Large-scale experiments on the fermentation of starch by a special ferment, yielding butyl alcohol and acetone, were begun in 1912, and the process was largely developed during the war. According to Tunison,[6] contamination difficulties in the fermentation process have only been successfully overcome during the last two years, and the increased production from this source is likely to reduce the price of acetone in future.[7]

Methyl Ethyl Ketone, $CH_3 \cdot CO \cdot C_2H_5$.—This substance is the homologue of ordinary acetone, which is dimethyl ketone, and is derived from the products of the distillation of wood. It has usually a pale yellow colour, which should not be too pronounced. Its

specific gravity varies from 0·810 to 0·815 at 15°, and on distillation 95% should distil between 70° and 81°. It should be miscible with an equal volume of benzene and with three volumes of water, and should be neutral and free from non-volatile impurity. The B.E.S.A. specification (2D. 1) includes a test for refractive index, solubility in a saturated salt solution, and content of ketone, determined by a titration method based on oxime formation with hydroxylamine hydrochloride. Methyl ethyl ketone always contains some acetone, which is estimated with it and calculated as methyl ethyl ketone. This explains why it is possible to fix the minimum content as high as 100%. Pure methyl ethyl ketone is not a solvent for cellulose acetate at ordinary temperatures.[4]

Methyl Acetone.—Methyl acetone is a crude fraction of wood distillate containing acetone and methyl alcohol as its principal ingredients. It varies very considerably in properties, as the following results of distillation will show :—

Range.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Up to 50°	a few drops	a few drops	a few drops	a few drops	a few drops
50—55	2%	2%	31%	2%	35%
55—60	44	54	49	36	54
60—65	49	34	15	6	9
65—70	4	9	4	11	1
Above 70	—	—	—	44	—

The colour is usually yellow or yellowish-green and the odour very rank. Sometimes both the colour and the odour improve slightly after an exposure to light for several days.

Higher grades can be obtained, however, and the material has been standardised by the British Engineering Standards Association (No. D. 2). It should be colourless or not darker than a faint yellow; 95% should distil between 50° and 70°. (It will be noted that all but No. 4 of the samples described above comply with this distillation test.) The acidity or alkalinity to phenolphthalein must not exceed 0·02%, and it must be miscible with water in all proportions or with its own volume of carbon disulphide at 25°.

This specification is of particular interest, as it makes use of a determination of solvent power number (*q.v.*). Two solutions are made up containing 6 grammes of cellulose acetate (D. 6), one with " pure dry acetone " and the other with the sample of methyl acetone under examination. A measured volume of each solution is placed in a flask immersed in a thermostat at 25°, and alcohol (2D. 9) is run

into each from a burette, with constant shaking, until a faint permanent opalescence is obtained. It is evident that if acetone is the better solvent, it will bear a greater dilution with alcohol than the methyl acetone before the cellulose acetate begins to precipitate; and that the solvent power is measured by the volume of alcohol added. If the acetone solution has taken a c.c. of alcohol and the methyl acetone solution b c.c. of alcohol, then

$$\text{Solvent power of sample} = \frac{b}{a} \times 100.$$

The material is graded according to the result of this test.

Grade I has solvent power not below 65,
„ II „ „ „ 50,
„ III „ „ „ 30.

Methyl acetone in Grade I must also contain at least 55% of acetone, determined by Messinger's method (*Ber.*, 1888, **21**, 3366).

It will be observed that the solvent power test only determines the value of methyl acetone as a solvent for cellulose *acetate*, and this is roughly proportional to its content in acetone. Since the other main ingredient is methyl alcohol, which is a solvent of nitrocellulose, methyl acetone is a better solvent for cellulose nitrate than for cellulose acetate. It is not a very desirable material, however, on account of its variability and its usually unpleasant odour.

Ethyl Alcohol, $C_2H_5{\cdot}OH$.—Ethyl alcohol, usually termed simply alcohol, and sometimes "spirit," is a constituent of nearly all cellulose nitrate lacquers, since they are made chiefly from nitrocellulose which has been dehydrated with alcohol. As is well known, it is produced by the fermentation of dextrose, derived either from starchy materials or from molasses. Other methods of manufacture, such as by the addition of the elements of water to the gas ethylene, $CH_2{:}CH_2$, have been and are being investigated, but have not yet had any influence on the market.

Alcohol for use in the manufacture of varnishes is denatured (rendered non-potable) by the addition of 5% of wood naphtha, and is bought free of duty as "Industrial Methylated Spirits." The presence of this quantity of wood naphtha, which is an impure form of methyl alcohol, confers slight solvent power on the alcohol. Alcohol should be colourless, free from appreciable non-volatile residue, and miscible with distilled water in all proportions. The concentration of alcohol is usually ascertained from its density, which is conveniently determined by a delicate hydrometer. A special form of hydrometer, known as Sikes's, is made for this

purpose, provided with a series of counterpoises by the use of which it is possible to measure with considerable accuracy the density of any concentration of alcohol from zero to 100%. If only strong alcohol is dealt with, this instrument is not necessary. The best specific gravity tables to consult in ordinary laboratory work are those of Thorpe.[8]

Industrial methylated spirit should have a proof strength of not less than 66 O.P., which denotes a liquid having a specific gravity of 0·8171 at 15·6°/15·6°, and containing 91·9% of ethyl alcohol (including the methyl alcohol used as denaturant) by weight, and 94·7% by volume. A higher specific gravity shows the presence of an excess of water, and such a spirit should not be accepted. Occasionally a somewhat stronger spirit with a lower specific gravity may be encountered, and is, of course, unobjectionable.

A distillation test should show a fraction of not less than 95% distilling between 76° and 79° at 760 mm. pressure, and the alcohol should be neutral in reaction. The B.E.S.A. specification (2D. 9) gives limits for acidity to phenolphthalein and alkalinity to methyl red, and states that the spirit should have an agreeable odour, a stipulation with which the Government Chemist would probably not agree.

Methyl Alcohol, $CH_3 \cdot OH$.—Methyl alcohol is a useful low-boiling solvent of the lower nitrates of cellulose. It is produced with other substances in the dry distillation of wood, and whether its solvent power is due to the presence of traces of acetone is a question that has never been authoritatively settled. At any rate the purest form occurring in commerce is a powerful solvent. This grade is seldom, if ever, used in varnishes, as it is dutiable. There is a lower grade usually sold as wood spirit, and the lowest grade of all is the so-called " miscible wood naphtha," selected for its nauseousness and used for the denaturing of ethyl alcohol (*v. supra*).

Wood spirit cannot usually be used for transparent or delicately tinted lacquers, as it is seldom free from colour and often colours still more strongly on exposure to light. If it is required for a purpose where colour is of importance, this property should be tested with the samples submitted. It should leave no appreciable residue on evaporation and on distillation should give 95% between 63° and 68°. The specific gravity 15°/15° should not exceed 0·810, and the spirit should be neutral.

It should be noted that both industrial methylated spirit (ethyl alcohol) and wood spirit (methyl alcohol) invariably contain a small

percentage of water, so that neither is miscible with petroleum spirit without cloudiness. According to Tunison,[5] the use of anhydrous ethyl alcohol for the manufacture of lacquers is being developed in the United States, with the object of reducing as far as possible the original water-content of the lacquer.

Ether.—Ether, or diethyl ether, $(C_2H_5)_2O$, is made by the interaction of sulphuric acid and alcohol; hence it is sometimes termed "sulphuric ether." It is not an important commodity in the varnish industry, as it enters only into the manufacture of the ether–alcohol collodions, which represent a very small proportion of the total output. In the explosives industry it takes a much more important place.

Ether is a colourless, mobile, volatile liquid, boiling at 34·5°, and is the most volatile solvent used in the industry. It is only partially miscible with water. The specific gravity of the commercial article varies from 0·72 to 0·73, according to the alcohol and water content. The specific gravity of pure ether is 0·7195 at 15°, and if the chief impurity is alcohol, a specific gravity of 0·730 corresponds with a material containing about 92% of ether, and a specific gravity of 0·720 with one containing 98—99% of ether. Anhydrous ether should show no cloudiness when mixed with an equal volume of carbon disulphide at 15°; the usual commercial article is miscible with alcohol, benzene and chloroform. Ether sometimes contains a small quantity of residue with an unpleasant odour, which is disadvantageous in collodion manufacture. This is most conveniently detected by allowing a few cubic centimetres to evaporate in an open dish.

Although ether is so volatile, its vapour is so heavy, on account of its comparatively high molecular weight, that it may travel along the ground for a considerable distance in sufficient concentration to propagate a flame. Hence special care must be taken both in manufacturing and applying solutions in which ether is used. Running motors are the most likely source of sparks near the ground, and these should not be used in the same room as ether.

Ethyl Acetate.—Ethyl acetate has hitherto been used much more in the United States than in this country, and Tunison [6] refers to it as the most important nitrocellulose solvent. It is now made in this country from industrial methylated spirit under special Customs regulation, and the consumer must give a guarantee that it will be used for solvent purposes only, and not for such purposes as flavouring, where it would displace a dutiable article. The following is a typical specification :—

It should be a clear, colourless liquid, with specific gravity at 15° not less than 0·890 or more than 0·900. 90% should distil between 70° and 85°. (The boiling point of pure ethyl acetate is 77°.) Its acidity calculated as acetic acid should not exceed 0·01%, and it should be miscible at 15° with double its volume of benzene. The ester content is determined by saponification with standard alcoholic caustic potash in the usual way and should not be less than 85% calculated as ethyl acetate.

Ethyl acetate has a higher specific gravity than ethyl alcohol (from which it is made) and a lower specific gravity than water. Hence a high figure for the specific gravity does not necessarily indicate a high ester content. It may indicate dissolved water and should be checked by the miscibility test. A low specific gravity usually indicates excess of unesterified ethyl alcohol.

The B.E.S.A. specification (D. 19) is less stringent than that just given in regard to acidity, as it fixes the maximum at 0·1%. It is more stringent in regard to distillation (95% between 70° and 80°) and ester content (90%).

A curious sample of American origin analysed in the writer's laboratory a few years ago gave an ester content of 93·4%, was free from water and satisfactory in regard to acidity. The distillation, however, gave only 71% up to 85°, 20% from 85—100°, and 7% from 100—113° (total 98%). Apparently the higher boiling fraction consisted chiefly of a homologous ester.

Butyl Acetate.—This material is displacing amyl acetate to a very considerable extent as the chief high-boiling solvent constituent of lacquers. This is largely due to its greater stability of price, since amyl acetate is generally to be preferred on account of its somewhat slower rate of evaporation and smaller affinity for water. It is made by the acetylation of butyl alcohol.

Butyl acetate should be a clear, colourless liquid, free from appreciable non-volatile residue and having a specific gravity at 15° between 0·875 and 0·880. On distillation 95% should boil between 110° and 130°. It should be miscible in all proportions with benzene, although the commercial article will sometimes turn cloudy with 4 volumes of petroleum spirit. The ester content should be at least 87·5% calculated as butyl acetate.

The B.E.S.A. specification is 2D. 4.

Amyl Acetate.—It was explained in an earlier chapter how the discovery by Stevens of the valuable properties of amyl acetate as a solvent for nitrocellulose laid the foundation of the lacquer industry. Unfortunately, ever since the rise of the cinema film industry, amyl

acetate, or rather the fusel oil from which it is made, has been a favourite commodity for the speculator. Its sole commercial source is as a by-product in the fermentation of sugar to alcohol and there is no competitive method of manufacture. The effect of the rapid fluctuations in price has been greatly to stimulate the manufacture of butyl alcohol and butyl acetate.

Technical amyl acetate should be a clear, colourless, neutral liquid, free from appreciable residue on evaporation. The percentage of ester calculated as amyl acetate should not be less than 90, and 98% should distil between 110° and 145°. The specific gravity should not be less than 0·870 nor more than 0·875; and the ester should be miscible with benzene or toluene in all proportions. The B.E.S.A. specification is a little stricter in regard to distillation ranges, which is laid down as 95% between 125° and 145°. In effect this reduces the permissible amount of lower homologues, derived from the presence of propyl and butyl alcohols in the original fusel oil.

Ethyl Lactate.—According to Tunison,[6] the use of ethyl lactate as a nitrocellulose solvent is increasing rapidly.

Technical ethyl lactate is a colourless liquid boiling from 145° to 155°, and its specific gravity is 1·037 at 20°. It is therefore somewhat heavier than amyl acetate, and evaporates more slowly. It will bear heavier dilution with water than most solvents without losing its solvent power. According to Gardner,[9] solutions of nitrocellulose in ethyl lactate have a rather higher viscosity than those of equal concentration in butyl acetate, and dry more slowly. They will, however, bear considerably more dilution with non-solvents such as benzene.

Acetone Oils.—The materials appearing in commerce under the name "acetone oil" are fractions, varying in composition, of higher boiling point than acetone, obtained in the wood distillation industry after the removal of the acetone. They consist of higher ketones, and a good sample may contain a considerable quantity of low-boiling ketones such as methyl ethyl ketone and methyl propyl ketone. Such solvents are known as light acetone oils and are useful in the industry. Heavy acetone oils are of much smaller value; not only do they dry very slowly, but the smell is sometimes difficult to tolerate.

No standard specification can be suggested, owing to the variability of the material, and acetone oil cannot be commended as a solvent for the same reason. All that can be said is that the value of the oil is governed chiefly by its content in low-boiling material, its

colour, and its odour, provided that the usual tests for neutrality and residue are satisfied. The acetone oils were first used in nitrocellulose lacquers by Crane.

Diacetone alcohol was patented by Doerflinger [10] in 1911 as a solvent for cellulose acetate and nitrate. It is prepared by the condensation of two molecules of acetone by sodium hydroxide, and has the formula

$$HO-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CO-CH_3,$$

and the boiling point is 164°. A sample examined in the writer's laboratory gave the following figures :—

Specific gravity at 15° 0·9037.
Completely miscible with water.
Distillation—

Up to 65°	5%
65— 80°	20%
80—140°	10%
140—164°	5%
164—170°	45%

The sample contained a considerable quantity of acetone. A solution of nitrocellulose in the sample gave a clear film on glass, which dried very slowly owing to the low vapour pressure of the bulk of the solvent. It is also a solvent of cellulose acetate, but has been used to a larger extent in the United States than in Europe.

Tetrachloroethane, $C_2H_2Cl_4$.—Tetrachloroethane is made by the combination of acetylene and chlorine. Acetylene tetrachloride and " westron " are synonymous. It has the somewhat high boiling point of 146°, and is a good solvent for cellulose acetate when mixed with alcohol. Its specific gravity is 1·6 at 15°. In the presence of moisture it is liable to develop traces of hydrochloric acid, and it should be tested by shaking it with water, acidifying the aqueous layer with nitric acid and adding silver nitrate. It is not a solvent for cellulose nitrate under any conditions, and is not an ingredient of the official cellulose acetate aeroplane dopes. The odour is characteristic and easily recognisable. Whenever it is used, special attention must be paid to the ventilating arrangements, as the continued inhalation of the vapour is injurious and a number of cases of toxic jaundice among workers in the aeroplane doping sheds in 1915—16 were traced to its use.[11]

Benzene, C_6H_6.—This is a coal tar distillate, to be carefully distinguished from benzine, a paraffin distillate. To prevent the confusion arising from the identity of pronunciation, the former is usually known by its commercial name benzol, and the latter is frequently called petroleum spirit. Benzene approximates to a pure aromatic hydrocarbon, C_6H_6, while benzine is a mixture of several homologous saturated hydrocarbons. Benzene forms with alcohol a mixture having weak solvent power for the lower nitrates of cellulose. Benzine is a non-solvent under all conditions.

There is no need to stipulate for a high degree of chemical purity in benzol required for varnish manufacture, since its next homologue, toluene, $C_6H_5{\cdot}CH_3$, is also a useful diluent which forms a similar solvent mixture when mixed with alcohol. If required for clear or delicately coloured lacquers, it should itself be practically colourless. It should be free from acidity, and should leave no appreciable residue on evaporation. Its specific gravity should be not less than 0·883 or more than 0·886 at 15°. When shaken with pure concentrated sulphuric acid it should not give more than a pale yellow coloration. The B.E.S.A. specification (2D. 10) limits the amount of carbon disulphide, and includes a test to prove the absence of paraffin hydrocarbons. Carbon disulphide is an unpleasant impurity, as it not only affects the workers using the lacquers, but may also tarnish metal work by forming metallic sulphides. In fact, a rough but useful test is to note the time for the development of a stain on a clean silver coin. Paraffin hydrocarbons may be present as adulterants, since they are cheaper than benzol, but the sulphonation test described is not necessary with every consignment from a reputable supplier.

Toluene, $C_6H_5{\cdot}CH_3$.—Toluene comes next to benzene in the series of aromatic hydrocarbons derived from coal tar, and the specification runs on similar lines. It can be obtained commercially in a high state of purity, perhaps higher than is necessary in the majority of varnishes. The distillation of such toluene should give at least 95% boiling between 110° and 112°. The specific gravity should be not less than 0·867, not more than 0·869 at 15°. The colour developed on shaking with concentrated sulphuric acid should not be darker than straw-yellow. Toluene was prepared on a large scale during the war by the fractional distillation of Asiatic petroleum. Toluene of this origin should be tested by the sulphonation test (B.E.S.A. 2D. 10) for the presence of saturated hydrocarbons.[12] This test is unnecessary for toluene derived from coal tar.

Commercial distillates can be obtained consisting chiefly of a

mixture of benzene and toluene, and these can frequently be used in varnishes. The specification in this instance should be based on a distillation test and specific gravity test, designed to limit undue variation in the proportions of the ingredients and hence in the rate of evaporation.

Butyl Alcohol.—Butyl alcohol is a useful modern addition to the ingredients of cellulose nitrate varnishes. Although not a solvent itself it forms solvent mixtures with organic esters and with aromatic hydrocarbons, and on account of its low vapour pressure it checks the rate of evaporation, thereby preventing the deposition of water, and producing a smoother and tougher film. It should be a clear colourless neutral liquid, having a specific gravity at 15° not less than 0·810 or more than 0·820. 95% should distil between 95° and 120°. The B.E.S.A. specification (D. 17) contains a determination of the percentage of butyl alcohol present, based on acetylation with pure acetic anhydride in a pyridine medium and titration of the acetic acid produced :—

$$(CH_3{\cdot}CO)_2{:}O + C_4H_9{\cdot}OH = C_4H_9{\cdot}O{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}COOH$$

This method is due to Verley and Bölsing,[13] whose original paper should be consulted. It is, of course, not specific for butyl alcohol. Spiers [14] describes a method of determination of butyl alcohol by fractional distillation.

Amyl Alcohol.—Crude amyl alcohol from the distilleries is known as fusel oil, and when purified by rectification is called amyl alcohol. These substances have similar properties to butyl alcohol, which is largely displacing them.

Both should be neutral colourless liquids. The specific gravity of fusel oil ranges from 0·813 to 0·820, and of amyl alcohol from 0·815 to 0·819. Fusel oil should distil between 125° and 132°, amyl alcohol between 128° and 132°. They should mix with an equal volume of toluene without cloudiness.

Triacetin is the triglyceryl ester of acetic acid,

$$\begin{array}{l} CH_2{\cdot}O{\cdot}CO{\cdot}CH_3 \\ CH{\cdot}O{\cdot}CO{\cdot}CH_3 \\ CH_2{\cdot}O{\cdot}CO{\cdot}CH_3 \end{array},$$

and is used as a softening agent both in cellulose acetate and in cellulose nitrate dopes, but chiefly in the former. The B.E.S.A. specification is 2D. 11.

Triacetin should be a clear, colourless liquid having a specific gravity at 15° not less than 1·16 nor more than 1·17. It should be

miscible with twice its volume of benzene at 0° without showing cloudiness (freedom from glycerin and water). The acidity should be less than 0·15% calculated as acetic acid. The makers will guarantee a maximum of 0·1%. The percentage of ester is determined by saponification with normal aqueous sodium hydroxide, and should be not less than 97% calculated as triactin.

Benzyl alcohol, $C_6H_5 \cdot CH_2OH$, is used as a high-boiling solvent and softener in cellulose acetate dopes, and occasionally in nitrocellulose solutions. It is made by the saponification of benzyl chloride, $C_6H_5 \cdot CH_2Cl$, and it must therefore be tested for free hydrochloric acid and for combined chlorine. The B.E.S.A. specication is 2D. 7.

Benzyl alcohol should be a clear, colourless liquid with a specific gravity at 15° not less than 1·050 and not more than 1·055. On distillation, 95% should be collected between 200° and 210°. Rather a higher tolerance than usual is allowed for non-volatile residue, namely 0·1 gramme (maximum) from 10 c.c. Free acid, calculated as benzoic acid, must not exceed 0·1%. It must give up no soluble chloride to distilled water on shaking. The chlorine content is determined by boiling under reflux with alcoholic potash and estimating the soluble chloride formed; this method assumes that the chlorine is present in a form removable by hydrolysis (*e.g.*, as benzyl chloride). Benzyl alcohol is determined by acetylation with acetic anhydride in pyridine solution (*v.* butyl alcohol).

Triphenyl Phosphate.—This material is used both as a softener and as a flame-resister in cellulose acetate dopes. It has rather an interesting history. It was patented as far back as 1901 by Zühl[15] as a substitute for camphor in ordinary celluloid, but was never used on the large scale. Shortly before the war it was adopted as a constituent of acetate dopes, and was manufactured in very large quantities for that purpose. After the war, attempts were made to work off stocks by using it as a camphor substitute in ordinary celluloid in accordance with Zühl's original patent, but it has several drawbacks, and its use for this purpose is diminishing. There is some conflict of evidence as to its solvent properties. For some varieties of nitrocellulose, a solution of triphenyl phosphate in ethyl alcohol has practically no solvent power whatever.

The B.E.S.A. specification is 3D. 12. Triphenyl phosphate should be a white, dry powder or crystalline substance, which should not darken on exposure to sunlight. It should be completely soluble in amyl acetate, butyl acetate, acetone, benzene and alcohol. The melting point should lie between 45° and 48°. The

acidity should be less than 0·01%, calculated as the equivalent of caustic soda. It should give a clear solution in chloroform (absence of water) and should be free from chlorides, sulphates and inorganic phosphates. The ash should be less than 0·05%.

Castor oil is a valuable softening agent for nitrocellulose coatings, since its solubility in alcohol facilitates its incorporation in solutions, and when of good quality it has only a faint yellow colour. The best oil is that known as " cold drawn."

The B.E.S.A. specification is 2D. 5. The specific gravity should be not less than 0·963 nor more than 0·966 at 15°. The free acid determined by sodium hydroxide titration with phenolphthalein as indicator, should not exceed 0·75%, calculated as oleic acid. The iodine value should lie between 84 and 89. The solubility test in alcohol described in 2D. 5 is useful, but it is not clear why it is entitled " Critical Solution Temperature in Alcohol," since no critical temperature is determined.

According to this test, 1 volume of the material should be completely soluble in 5 volumes of 59·6 O.P. alcohol at 20° and the solution should remain clear when cooled to 0°. (59·6 O.P. alcohol has the required specific gravity of 0·8303 at 60° F.) The refractive index at 20° should lie between 1·4772 and 1·4791.

(*Note.*—The miscibility test described above appears to be based on that of Finkener. Archbutt and Deeley [16] recommend a variation of this test which has been of considerable service in the writer's laboratory :—" Measure exactly 10 c.c. of castor oil in a graduated stoppered test cylinder, add 50 c.c. of alcohol of specific gravity 0·834 (= 89·9% by vol. = 57·6 O.P.) and well mix. If as little as 5% of foreign oil be present the liquid will remain strongly turbid even on warming to 20°.")

Castor oil is an expensive material, and unless it is bought from firms of the highest standing, adulteration is not uncommon. In doubtful instances it will be found useful to consult Lewkowitsch.[17]

Resins.—The chemistry of the resins is unusually complicated, and for fuller details than can be given here, the reader is referred to the literature mentioned in the bibliography.

Resins are incorporated with nitrocellulose varnishes for the purpose of increasing the body or solid content, and producing a harder, more elastic and more adhesive coating. The presence of the nitrocellulose renders the film tougher and more resistant than one derived from resins alone. The resins chiefly used in the industry are shellac, mastic, copal, sandarac, and dammar.

Shellac.—Shellac resin is the secretion of the lac insect, indigenous to India, and the production of shellac is an important

native industry in that country. It is a valuable resin on account of its hardness, adhesiveness and elasticity. The standard grade is that sold as ◇TN◇, which usually contains 3% of added rosin. Garnet lac, which has a deeper colour, may have 10% of rosin, while the form known as button lac, consisting of small plates or discs of the resin, varies in composition from pure shellac to a product which is about half rosin. The addition of rosin (a cheap rosin which forms the residue from turpentine distillation) was at one time thought to assist the manufacture, and although it is no longer necessary, the existence of the adulteration is recognised in the industry. A bleached shellac is made by the action of alkaline hypochlorite on shellac. It is much paler in colour than ◇TN◇ shellac, but more friable and not quite so soluble in methylated spirit.

Shellac contains about 4% wax (insoluble in alcohol), the remainder being the resin. Garnet lac is free from wax and therefore gives a clear solution in alcohol, but against this advantage must be placed the higher percentage of adulterant.

The pure resin is soluble in ethyl alcohol, methyl alcohol and amyl alcohol; partly soluble in ether, ethyl acetate and acetone; only slightly soluble in benzene, toluene and petroleum spirit.

Mastic.—Mastic resin (commonly called gum mastic) is an exudation from a tree growing abundantly on the shores of the Mediterranean. It is a hard resin, but softens below 100°, and is pale yellow or greenish in colour. It is completely soluble in amyl alcohol, benzene and ether and partly soluble in most of the other usual ingredients of nitrocellulose varnishes, but is insoluble in petroleum spirit. It is, however, difficult to blend with solutions of other gums or with nitrocellulose on account of a tendency to precipitate, and considerable experience is necessary to obtain satisfactory results. It is sometimes adulterated with rosin or sandarac resin, as it is an expensive material.

Copal.—Copal is the name given to a large variety of tropical resinous products, the best and hardest being of fossil origin. It occurs in East and West Africa, the East Indies, New Zealand and parts of South America. The colour varies from red to yellow. Zanzibar (East African) copal is usually considered the best, and New Zealand (kauri) is also very good. The best and hardest varieties, however, are not used in nitrocellulose varnishes, on account of their poor solubility. Softer copals are more soluble. For example, Zanzibar copal may contain 80—90% insoluble in alcohol, while the softer Manila copals are soluble to the extent of

about 95% in alcohol, and also dissolve in amyl alcohol and in amyl acetate.

Sandarac.—Sandarac is the resin derived from a tree flourishing in north-west Africa, and another variety comes from Australia. It is a yellow, somewhat friable resin, occurring in commerce in small pieces or transparent drops of a yellow colour. It is soluble in ether, ethyl alcohol, acetone and amyl alcohol, but only partially soluble in benzene, toluene and petroleum spirit. It is moderately hard, and is used in the preparation of negative and label varnishes.

Dammar.—Dammar is obtained from various trees growing in the Federated Malay States, Sumatra and the Dutch East Indies. It is a fairly hard resin, but it softens considerably below 100°. It is completely soluble in benzene and in oil of turpentine, and nearly so in ethyl alcohol. It is partially soluble in ether and acetone.

The resins show some properties resembling those of the cellulose esters, particularly in regard to their solubility relations. They are frequently more soluble in a mixture of two liquids than in either alone, and this fact must be kept in mind in consulting the published information on their solubility data.

Esselen notes that when lacquers are made up from solutions of cellulose esters and resins, the finished product is different according to whether the cellulose ester or the resin is added to the solvent. In some instances, if the resin is dissolved in the solvent first, the cellulose ester will not dissolve, while if the ester is added first, the resin will easily dissolve afterwards. He suggests that the cellulose ester and the solvent together form the dispersion medium, and the resin the disperse phase.

The proportions in which the resins are used differ very considerably, according to the purpose for which the varnish is required. A typical formula given by Field, the originator of this kind of lacquer, was :—

Amyl acetate	50 gallons (U.S.)
Oil of turpentine	25 ,,
Methyl alcohol	25 ,,
Nitrocellulose	37·5 lb.
Shellac	37·5 ,,

Worden remarks that the turpentine was omitted later, on account of its slow-drying properties.

Two other formulæ may be quoted from Worden to illustrate the use of the resins. Both are for bronze paints having moderate resistance to heat, and therefore suitable for low-temperature radiators and hot water pipes.

	Formula 1.	Formula 2.
Amyl acetate	40—50	35—45
Amyl alcohol	4—5	20—30
Wood spirit	35—50	15—25
Petroleum spirit	35—50	30—45
Boiled linseed oil	—	4—6
Nitrocellulose (not defined)	2·75	3·0
Mastic	1·5	—
Copal	—	4·0
Aluminium and bronze powder	(added before use)	10·0

The increased proportion of amyl alcohol in the second formula is probably necessary to keep the copal in solution, and the use of linseed oil is said to diminish the tendency of the paint to gelatinise, a drawback of bronze mediums to which reference will be made (p. 132). On the other hand, the addition of linseed oil diminishes the rate of drying considerably, and the film from such a solution will feel tacky long after one from a solution similar to formula 1 will have set hard.

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British Engineering Standards Association Specifications.

Methyl Ethyl Ketone, 2D. 1. Butyl Acetate, 2D. 4. Castor Oil, 2D. 5. Benzyl Alcohol, 2D. 7. Nitrocellulose Syrup, 2D. 8. Alcohol, 2D. 9. Benzol, 2D. 10. Triphenyl Phosphate, 3D. 12. Acetone, 2D. 22. Cellulose Acetate, D. 50.—To be obtained from the Secretary of the Association, 28 Victoria Street, Westminster, S.W. 1., price 2*d.* post free.

CHAPTER VIII

MANUFACTURE AND APPLICATION

Manufacture of the Varnishes—Mixers—Measurement of Ingredients—Addition of Solvents to Esters—Incorporation of Pigments—Clarification and Filtration—Aeroplane Dopes—Effect on Strength of Fabric—Composition of Dopes—Doping Schemes—Method of Application—Discussion of Typical Dopes—Differences in Allied Practices—Protection from Sunlight—Metal Coatings—Application by Brushing, Dipping and Spraying—Transparent Lacquers—Enamels—Aluminium and Bronze Mediums—Motor-car Enamels—Imitation Leather—Leather Dressing—Patent Kid—Patent Leathers—Treatment of Motor-car Upholstery Leather—Coatings for Wood, Paper—Preservation of Antiques—Miscellaneous Applications—Collodion.

Manufacture of the Varnishes

THE varnishes are made in any convenient type of mixing apparatus. Enclosed mixers provided with stirring blades are very efficient. Various types of revolving churns can be employed, or earthenware or lead-lined vessels with metal or wooden stirrers. Rapid stirring is neither necessary nor desirable, as the rate of dispersion of the esters is slow. Since in all instances some at least of the solvents are highly volatile, the mixer must be built as airtight as possible to avoid loss of solvent and change of composition during mixing. It is advantageous if the mixer can be easily cleaned, but it is preferable to use a separate mixer for solutions of each colour. If it is ever necessary to use a machine for an entirely different colour from that for which it has previously been used, it should be cleaned out by hand as completely as possible, and then washed out for several hours with a strong solvent mixture.

The solid constituents of the varnish are weighed out. Cellulose acetate is usually weighed dry. Cellulose nitrate is generally weighed wet with alcohol from the dehydration process. The required weight must then be calculated from the laboratory determination of the amount of dry ester in the sample, and the quantity of alcohol in the ester must be deducted from the quantity indicated by the formula, when the liquid ingredients are added.

The liquids are usually measured by volume, although, owing to their high coefficient of expansion, this method is not very accurate unless the temperature of the shop is moderately constant. There is a great deal to be said for measuring all the liquid ingredients by weight. Unfortunately, there is no uniformity of practice in the trades dealing in solvents. The tendency is for the cheaper liquids, alcohol, benzene, toluene, xylene and petroleum spirit, to be sold by the gallon, and more expensive liquids, such as acetone, ethyl, butyl and amyl acetates, by the ton. If they were all sold by weight, the varnish manufacturers would probably adopt the

same system and ensure, not only a more accurate and uniform manufacture of their goods, but also considerable simplification in their stock-taking and book-keeping.

It is sometimes good practice not to add all of the solvent mixture to the cellulose ester at one time. No general rule can be laid down, but there is frequently a saving in time if the whole of the non-solvents (if any) and only a part of the true solvents are placed in the mixer at starting. The remainder of the true solvent is added at intervals determined by experience. There are two possible explanations of the saving of time which sometimes results from this procedure. In some, in fact in most instances, the " non-solvents " include ingredients which increase the solvent power of the true solvents. These ingredients diffuse rapidly into the ungelatinised ester, probably causing it to swell without dissolving, and this may assist the later penetration of the true solvent. There may also be a physical disintegration of the ester when the composition of the liquids is just approaching the point at which they become a solvent, and such disintegration will expose a large surface to the action of the solvent. This may be illustrated on a laboratory scale by shaking cellulose nitrate with aqueous acetone containing enough water to possess no solvent action. If the proportion of acetone is gradually increased, a stage is reached at which the cellulose nitrate disintegrates to a powder, and the continued addition of acetone leads to rapid dispersion. On the other hand, when pure acetone is used as the solvent, it is difficult to prevent the formation of large clots, enveloped in gelatinised ester, and exposing so little surface to the action of the solvent that dispersion is greatly delayed.

No general rule can be laid down as to the time required for the manufacture of cellulose ester solutions, since this varies according to the viscosity of the cellulose ester, the nature of the solvents, the order in which they are added, the final concentration and the temperature of the shop. Usually, however, batches begun on one day and kept in movement overnight are ready the next day. Pigmented varnishes (enamels) may be made directly from pigmented celluloid, by dissolving the celluloid in an appropriate mixture of solvents. Celluloid, however, is made from a cellulose nitrate of high viscosity, and a solution made from it will yield a thinner coating for the same consumption of solvent than one made from an ester of low viscosity. Another property of varnishes made directly from celluloid which may be disadvantageous is their comparative softness arising from the presence of camphor.

When enamels have to be made from the nitrocellulose base, great care is needed to ensure the complete incorporation of the pigment. A mere stirring of the pigment into the finished solution is rarely successful; the particles of pigment tend to adhere together and " ball up," so that they do not disperse uniformly in the solution. The film from such a solution, whatever the solvent, will be rough and gritty, and the pigment will rapidly settle out of the solution on standing. It must be remembered that to ensure that every particle of pigment is surrounded by an envelope of solution requires the performance of a considerable amount of work against surface tension, and this work cannot easily be done by stirring. To obtain a satisfactory result, the solution and pigment should be ground together in a ball mill, preferably with porcelain balls, or the ester should be gelatinised with part of the solvent and ground on steel rollers with the pigment. The latter process is expensive in solvent, since there is a considerable amount of evaporation during the grinding.

Clarification of the Varnishes.

Solutions of commercial nitrocellulose or cellulose acetate are never quite transparent, owing to the presence of undissolved fibres, clots or adventitious impurities. For many purposes, the presence of a small quantity of insoluble matter does not affect the usefulness of the varnish. In making enamels, for example, the process of grinding in the pigment comminutes the impurities also, and any kind of clarification is unnecessary. Sometimes, however, it is necessary to obtain solutions of high transparency, and some treatment is necessary.

According to Kirkpatrick,[1] in the Parlin works of E. I. du Pont de Nemours and Company, filtration is carried out in frame filter-presses, through filter-paper backed with a heavy canvas filter-cloth. This process is only feasible when the solution to be filtered is of low viscosity, and even then it is advantageous to allow some of the insoluble material to settle by standing. A solution of high viscosity filters with extreme slowness through a press even when free from gelatinous impurities. The cellulose ester solutions, however, always contain impurities of a fibrous nature, frequently swollen by the action of the solvent mixture, and these felt together and form an increasing hindrance to the filtration.

The impurities in cellulose ester solutions can be thrown out satisfactorily by treatment in a centrifugal machine, but unless special precautions are taken there is a heavy loss of solvent during the process on account of the rapid movement of air over the surface.

The method which gives the most satisfactory results is undoubtedly settling under the influence of gravity. This is simply carried out by allowing the solution to stand in tall, narrow, cylindrical vessels, preferably of earthenware, until the impurities have fallen to the bottom. Where special transparency is required this process may take weeks or months. The disadvantages are (1) that losses by evaporation may be heavy unless strict precautions are taken, (2) that a great deal of money is locked up while the settling is taking place. Clément and Rivière [2] state that solutions settled in this manner for eight months are optically pure. The writer cannot quite confirm this, but the path of a beam of light through such a solution is certainly very nearly invisible. On the other hand, solutions clarified by filtration, and especially by centrifugal treatment, give an unsatisfactory optical test, and will sometimes, on standing, deposit a flocculent gel which will take longer to settle out completely than the original impurities which have been removed. Apparently in the clarification of these solutions time is a factor which cannot be completely ignored. For general purposes, however, optical purity is not required in varnishes, and subject to the criticisms made above, filtration and centrifugal treatment are satisfactory.

Ayres [3] mentions an instance of a nitrocellulose lacquer, which contained a cloud of finely-divided cellulose impurities, being filtered satisfactorily after the addition of a small percentage of tricalcium phosphate precipitated in alcohol. Other filtering agents, such as kieselguhr, fuller's earth, bone black, and barium sulphate, were found useless.

Applications of Cellulose Ester Varnishes.

Aeroplane and Airship Dopes.

The properties required in an aeroplane dope are that it shall increase the tensile strength of the fabric on which it is deposited, and cause a permanent increase in the tension. It should possess maximum resistance against water, oil and petrol, it should protect the fabric against the destructive effect of strong sunlight and atmospheric exposure, and it should be incombustible.

It has already been pointed out in an earlier chapter that the need for fulfilling the last condition has led to the adoption of cellulose acetate rather than nitrate as the basis of aeroplane doping systems.

Dopes for use on the fabrics of machines lighter than air should

possess the additional property of being impermeable to gases, and they should be poor conductors of heat.

Clément and Rivière,[2] who have made a special study of the mechanical properties of doped fabrics, give the following figures to show the order of increase in strength brought about by doping. The figures refer to breaking strain calculated per linear metre of the fabric; the thickness is not stated :—

Material.	Warp.		Weft.	
	Before coating.	After coating.	Before coating.	After coating.
Linen	1,730 k.	1,860 k.	1,800 k.	2,660 k.
Cotton	940	1,080	1,010	1,180
Silk	1,200	1,500	1,490	1,740

A number of tables are given by Ramsbottom [4] in the Technical Report of the Advisory Committee for Aeronautics for 1913–14, from which the following is taken :—

Tests on dope A.	Fabric before doping.	Fabric with 1 coat dope.	Fabric with 3 coats dope.	Fabric with 5 coats dope.	Fabric with 7 coats dope.
Weight, gms./m.^{2}	138·5	160	198·5	249	312·5
,, dope/m.^{2}	—	(21·5)	(60)	(110·5)	(174)
Strength, k./m.	1275	1523	1575	1730	1775
Increase in strength due to dope, k./m.....	—	248	300	455	500
Specific strength of fabric...	9·2	9·5	7·95	6·7	5·7
Specific strength due to dope	—	11·5	5·0	4·1	2·87

These tests are made in the direction of the warp only, as the fabric is more uniform in that direction. The results given on the last line for the specific strength due to the dope were calculated to show what is the increase in strength for a given added weight of dope. The values represent :—

$$\frac{\text{Increase in strength (kilos/m.)}}{\text{Weight of dope (grammes/m}^2\text{.)}}$$

They show that the influence of successive coatings of dope becomes rapidly less, so that a compromise is adopted between the standard of strength required in the coated fabric, and the weight of the fabric.

According to Drinker,[5] the fabrics used by the Allies for aeroplanes during the war were :—

Great Britain	Irish linen, cotton.
United States	Mercerised cotton.
Italy	Silk.
France	Silk and cotton.

Composition of Aeroplane Dopes.

The French air service used acetate dopes on all their aeroplanes. The British used a nitrocellulose dope on aeroplanes used for training, and on the war machines an acetate dope with a final coating of nitrocellulose varnish to protect the under-coats from the action of light.

If a dope is made up from cellulose acetate dissolved only in volatile solvents, it dries with considerable contraction to a hard film, which easily cracks. It is possible to introduce high-boiling softening agents into the solution which counteract this hardness, and produce a flexible film, at the expense of the contractile power. Since the fabric is stretched tightly on the frames before it is doped, only a moderate degree of contraction is necessary in the dope. It is therefore possible to incorporate a certain amount of a softener and thereby increase the resistance of the film to sudden shock. Of the softeners used the most important are triphenyl phosphate, tricresyl phosphate, phenol, acetanilide, methyl acetanilide, triacetin, benzyl alcohol.

A large number of softeners were tried during the war, but owing to their high price the use of many of these has been discontinued.

Non-inflammability.

The term non-inflammable is a somewhat vague word applied to those substances which do not burn freely. Cellulose acetate is a non-inflammable substance, so called because if in the massive form it is ignited, the flame usually expires as soon as the source of heat is removed. It must be remembered that the property of non-inflammability depends to some extent on the physical state of the material. Cotton wool, for instance, is an inflammable material; but a highly compressed bale of cotton or cotton paper in the form of a book would be difficult to ignite.

The term incombustible is reserved for substances having a higher degree of non-inflammability. Even this term is perhaps

only relative, but in common language it is applied to those substances which exhibit no fire risk whatever.

Although cellulose acetate is non-inflammable it is not incombustible, and when applied to a fabric in conjunction with an organic "softener," the fire risk may become sufficiently great to become a danger on aeroplane fabrics. It is usual, therefore, to incorporate some substance which will reduce the inflammability of the film to a state approaching incombustibility. Triphenyl phosphate is the material most commonly used for this purpose. It combines the functions of softening agent and reducer of inflammability. Although it contains a considerable percentage of carbon, the phosphate residue is an efficient check on combustion.

Application of Dopes.

British practice in the application of cellulose acetate and nitrate dopes is described in the following specifications issued by the British Engineering Standards Association.*

2D. 101, Feb. 1923, "Properties of Aeroplane Doping Scheme."
2D. 104, Dec. 1922, "Air Ministry Doping Schemes."
4D. 100, Feb. 1923, "Air Ministry Cellulose Acetate Dopes."
D. 23, July 1918, "Nitrocellulose Syrup for the Manufacture of Dope."
D. 102, June 1918, "Nitrocellulose Dope."
2D. 103, March 1922, "Air Ministry Nitro Dope Coverings and Identification Colours."
D. 105, Feb. 1923, "Pigmented Nitrocellulose Dopes for Use on Aeroplanes."

These valuable publications should be consulted by anyone interested in the application of cellulose ester varnishes, whether in reference to aeroplane protection or not, as many useful hints are given and tests described. Only a brief summary with comments can be given here.

2D 104 describes the purpose of the doping schemes, namely, the production of a taut, smooth, air-tight surface. Special coatings are required for protection of the doped fabric from light, for increasing the reflection of heat and light rays, and for better protection from observation during night flying. Directions are given for the application of the dope, which follow closely the usual practice in the industry. The shop should be dry and at a

* To be obtained from the Secretary of the Association, 28 Victoria Street, Westminster, S.W. 1, price 2*d.*, post free.

fairly constant temperature of 65–70° F. Humidity, or the prevalence of cold draughts, causes " blooming " of the films through the deposition of moisture. The standard of ventilation is a high one, namely, that the air should be completely changed thirty times per hour. This standard was laid down after the exhaustive investigation into the subject of ventilation carried out as the result of the mishaps with tetrachlorethane in 1915–16 (*v. supra*).

The dope is applied with a flat brush of stiff bristle, and the first coat must be well pressed into the fabric. The fabric must not be damp or cold. It must be free from weaving defects, and should be lightly and evenly stretched on the frames. It has been already pointed out from Ramsbottom's figures that the first coat gives the greatest proportionate increase in strength. This is doubtless due to the penetration of the dope into the fabric in such a way as to surround the fibres. A minimum of one hour is allowed before the next coat is applied. Usually in the industry a longer time than this is given, particularly when the solution is brushed on, as there is a great tendency for the second coat to disturb the first. Brush-work with cellulose ester varnishes is entirely different from brush-work with turpentine-linseed oil paints. The rate of evaporation is very rapid, and there must be no attempt at smoothing-out. The planes are doped preferably in a horizontal position, which favours an even application, and the brush should move in the direction of the strands of the fabric.

The allowance of dope per 100 square yards of fabric (not including waste) is from 14 to 18 gallons, for four coats, which corresponds with rather more than 2 oz. per square yard when the volatile solvent has evaporated.

2D. 101 defines four classes of doping schemes, the requirements of a dope being that it must tauten the fabric, protect it from injurious light rays and from moisture. Different schemes are possible according to whether those requirements are met by one dope or different combinations of two dopes. This specification describes useful tests for determining tautening properties, adhesion, elasticity, brittleness, weight, inflammability and rate of burning.

4D. 100 gives the formulæ of four different types of cellulose acetate dope, namely :

(1) A clear dope for use in temperate climates (A.D.)
(2) ,, ,, ,, ,, ,, tropical ,, (A.D.T.)
(3) ,, pigmented ,, ,, temperate ,, (A.D.P.)
(4) ,, ,, ,, ,, ,, tropical ,, (A.D.P.T.)

It will be worth while to consider one of these specifications in some detail, as it will show how much standardisation is necessary in order to ensure practical uniformity in the dope.

The formula for dope A.D. is as follows :—

Cellulose acetate	75 lb.
Acetone	60 gallons.
Methyl ethyl ketone	10 ,,
Alcohol	14 ,,
Benzol	14 ,,
Benzyl alcohol	2 ,,
Triphenyl phosphate	15 lb.

The literature of cellulose esters abounds with formulæ stated in a similar form to this, and most of them are almost worthless, because the properties of the ingredients are not defined. In this instance, however, every one of the ingredients has been standardised by previous specifications. Leaving out what one may call the obvious limitations on acidity, basicity and non-volatile residue on evaporation, these previous specifications fix the following properties on which the behaviour of the dope entirely depends :—

(1) Cellulose Acetate. The required solubility of this material in a test solvent made up in the same proportions as in dope A.D. has been strictly defined (2D. 50), and, most important of all, the viscosity of this solution between narrow limits.

(2) The five liquid solvents, acetone, methyl ethyl ketone, alcohol, benzol and benzyl alcohol, have all been specified in regard to allowable water content, specific gravity and range of boiling point. These determinations limit the amounts of impurities which might otherwise be present in commercial materials, and therefore ensure to a satisfactory degree that the viscosity of the dope when made up will fall between the same limits as were observed in the sample.

(3) The specification for the triphenyl phosphate employed ensures uniformity in the hardness of the film produced and in the degree of combustibility.

Without the rigid specification of all these ingredients, the final dope might vary so enormously in its properties that it would be entirely a matter of chance whether it would be suitable for the purpose in view.

It will also be of interest to consider the same formula in relation

to the boiling points of the volatile solvents, as these will give an approximate idea of the changes occurring during evaporation :—

Ingredient.	Quantity.	Range of B. p.
Acetone	60 gall.	95% from 55° to 60°
Methyl ethyl ketone	10 ,,	95% ,, 70° to 81°
Alcohol	14 ,,	95% ,, 76° to 79°
Benzol	14 ,,	95% ,, 75° to 85°
Benzyl alcohol	2 ,,	95% ,, 200° to 210°
Triphenyl phosphate	15 lb.	M. p. 45° to 48°

In the first place it must be noted that two of the ingredients, alcohol and benzol, are, when taken alone, non-solvents of cellulose acetate, even when hot. When mixed together, however, although they are still non-solvents in the cold, they form a solvent mixture on warming. Evidently therefore they are of more value when present together than either would be if present alone. In the next place, the most volatile constituent is evidently the acetone, and this will evaporate at a faster rate than the other constituents. It is, however, present in much larger quantity than the others, so that acetone is likely to be present in slight excess right up to the end of drying. Alcohol and benzol, which are chiefly of value when present together, and which have approximately equal rates of evaporation, are included in equal proportions, and their total volume, 28 gallons, is sufficiently small to ensure that they will not be left in excess when the true solvents have evaporated. The methyl ethyl ketone helps to diminish the rate of evaporation of the solvents, and in the presence of acetone is itself a strong solvent. It will be noted, however, that practically all of the volatile solvents boil below 85°, and that there is nothing intermediate between these and the benzyl alcohol, which will be left when the former have evaporated. The vapour pressure of benzyl alcohol at ordinary temperatures is extremely small so that its rate of evaporation is low, and it is left almost intact in the film with the non-volatile triphenyl phosphate.

This is a comparatively simple formula to study in this way, owing to the large excess of strong solvents in it. When the proportion of non-solvents or latent solvents is higher, it becomes much more difficult to forecast what is likely to happen as the solvents evaporate. Skill in this exercise is of great assistance in the preparation of new formulæ.

2D. 103 specifies various nitrocellulose dope coverings, applied

for protective coverings over acetate dopes. One of these may be examined in a similar way :—

Transparent Covering V. 114

260 lb. of Nitrocellulose Syrup 2D. 8	Nitrocellulose	52 lb.
	Alcohol	26 ,,
	Butyl acetate	182 ,,
	Butyl or amyl acetate	18½ gallons.
	Alcohol	22½ ,,
	Benzol	22½ ,,
	Castor oil	77 lb.

It will be noted that this formula involves a previous specification 2D. 8 in which the quantities are expressed by weight. The reason for this is that the nitrocellulose syrup is highly viscous and difficult to measure by volume.

The same remarks apply to this formula as to the previous acetate dope formula. It would be valueless for its purpose if the solubility of the cellulose nitrate, and its viscosity in the specified solvents, were not fixed within narrow limits, and if the proportion of the solvents were not defined so as to exclude the presence of impurities which even in small quantities might have a marked effect on the properties of the dope.

The boiling points of the ingredients may be tabulated in the same way :—

Ingredient.	Quantity.	Range of B. p.
Butyl acetate	38½ galls.	95% from 100° to 130°
Alcohol	26 ,,	95% ,, 76° to 79°
Benzol	22½ ,,	95% ,, 75° to 85°
Castor oil	77 lb.	

This is an even simpler mixture than the last. The non-solvents are again alcohol and benzol, but they form a solvent when mixed. Alcohol also assists the solvent power of butyl acetate. Benzol is the ingredient present in smallest amount, and there is no risk of it being present in excess at any stage of the evaporation. If amyl acetate is used instead of butyl acetate, the rate of drying will be somewhat slower.

Castor oil, being non-volatile, is entirely left in the nitrocellulose coating of which it will form more than half.

Note on Bibliography.

Interesting comparisons between the practice of various countries are given in the papers by Drinker [5] and by Clément and Rivière.[2] The Germans used lighter dope films than the Allies, the weight of dope being usually from 1 to 1·5 oz. per square yard, whereas British experience preferred a coat of 2 oz. The formation of white patches during doping, known as " blushing " in the United States and as " blooming " in this country, was due to the use of damp or draughty shops for the doping process. There is a very high percentage of low-boiling solvents in the standard aeroplane dope and very considerable cooling takes place as the solvents evaporate. Hence there is every probability of an excess of moisture depositing on the film and precipitating the cellulose acetate unless special precautions are taken to keep air dry. In this country, where doping processes and shops had to be hurriedly improvised, it was not possible to insist on the control of humidity in the doping sheds, but in the United States advantage was taken of the experience of the Allies and such control was enforced.

Although some experimental work was carried out on doping by means of a spray, or air-brush, the process was carried on by hand-labour throughout the war.

In French practice, the first or " scratch " coat contained only from 3–5% of cellulose acetate, and was made up with a high proportion of low-boiling solvent in order to give a greater tautening effect on the fabric. The second and third coats contained from 8–9% of acetate, with 2% of mineral pigments or metallic powders. Either eugenol or triacetin was used as the softening agent in these coats. The last coat was made with 8% acetate, and with a solvent having a high proportion of low-boiling solvent, as in the first coat. The French used chiefly methyl acetate as low-boiling solvent, and the British chiefly acetone, but the British Air Ministry endeavoured to minimise the consumption of products of wood distillation by the use of alcohol and benzene as diluents.

The French dopes did not contain triphenyl phosphate, but employed a variety of other softeners such as eugenol, benzyl alcohol, triacetin and glyceryl benzoate. None of these had a fire-resisting action similar to that of triphenyl phosphate. The Italian used a small percentage of phenol as the softening agent. The United States service used in the first coat a small percentage of phenol or naphthalene, and also an ant-acid, either urea or dicyandiamide. Three additional coats were put on, which con-

tained 7% of diacetone-alcohol to prevent "blushing," and small quantities of benzyl acetate or benzyl benzoate as softening agents.

The destructive action of sunlight on aeroplane fabric was investigated by Aston [6] (of isotope fame) and was found to be due chiefly to ultra-violet light in the region of the spectrum lying between 2950 and 4000 $\mu\mu$. These rays could be absorbed by certain pigmented coatings, and a special protective dope was developed known as PC 10. The pigment in this covering consists of a mixture of yellow ochre and carbon black, in a nitrocellulose and castor oil medium.

The various pigments employed to produce the colours used on British aeroplanes for the purposes of identification and protection are detailed in B.E.S.A. 2D. 103. Dopes which gave a matt black surface were adopted in France, at the suggestion of Clément and Rivière,[2] for machines used for night-bombing, and were almost invisible in the beam of a searchlight. Later suggestions from the same source were "clair de lune," blue-violet and deep red.

Metal Coatings.

The application of special enamels made from nitrocellulose of low viscosity to motor-car bodies, as has already been pointed out, is a recent development which has taken place only in the last two years. For many years, however, an industry has flourished in the protection and decoration of small metal articles with nitrocellulose lacquers. The use of lacquers and enamels of higher viscosity results in thinner coatings for the same consumption of solvent, or, conversely, a large number of applications to produce a thick coating. As most of the articles so coated are intended only for indoor use, where they do not encounter severe weather conditions, a thin coating is generally adequate for the purpose in view.

There are three general methods of application, (1) brushing, (2) dipping, (3) spraying.

Brushing is the least satisfactory process. Nitrocellulose lacquers dry so rapidly that any attempt to smooth out brush marks generally defeats its purpose. If used for a second application, it invariably disturbs the first coat, and the lacquer rapidly becomes sticky enough to draw bristles from the brush. Nevertheless, it may sometimes be necessary to apply a lacquer or enamel to a surface too large to be dipped conveniently, and in a situation where a compressed air spray is not available. Under these circumstances,

fair work may be done if the operator resolutely banishes from his mind all preconceived notions derived from the application of ordinary linseed oil paints or varnishes. The lacquer should be quickly applied to the surface without brushing out, keeping the brush well moistened. Whenever work is stopped, if only temporarily, the brush should be immersed in a solvent mixture to keep it from drying out. Lacquers intended for brushing require a higher percentage of high boiling solvent, so as to delay the rate of drying.

Dipping is a very satisfactory method of coating small articles. The lacquer is placed in a receptacle of convenient size, and the article is completely immersed and withdrawn. It is allowed to drain for a few seconds and is then transferred to a rack to dry. The two chief precautions to be taken are (1) to immerse the article in such a way that no bubbles of air are drawn under the surface; the procedure depends on the shape of the article and can usually be determined after one or two experiments; (2) to drain the article in such a way that no " drip " is formed at corners or edges; in some cases it may be advisable to apply a slow rotation mechanically to the articles while drying. A recent patent taken out by B. D. Baker [7] claims that drip may be avoided by hanging the articles in a vessel of the lacquer, and slowly drawing off the lacquer from the bottom of the vessel.

Spraying is a comparatively modern development, and is carried out with apparatus similar to that used in painting. Various types of air sprays are on the market, such as the Aerograph and the Aerostyle. The principle of the apparatus is that a fine jet of air under somewhat high pressure draws the lacquer from a reservoir by its injector action, and propels it in the form of a fine spray towards the article to be coated. In some instances, the reservoir feeding the spray is also under pressure. The conditions which may be varied are the pressure of the air, the viscosity and composition of the lacquer, the ratio of air to lacquer, the temperature of the workshop and the distance of the spraying apparatus from the work. Most of these are under the control of the operator, but the composition of the lacquer is the concern of the manufacturers. The latter can, however, assist the operator by supplying the lacquer in a slightly more concentrated form than is required for the spray, and supplying separately a " thinnings " or diluent, consisting of solvent only, which may or may not have the same composition as the liquid solvent in the lacquer. A few trials will usually show what is the best proportion in which to mix the lacquer and the

thinnings, and great care should be taken to ensure that the two are thoroughly mixed.

Flowing is really a variant of the dipping process, and is sometimes convenient when large articles are to be covered. The lacquer is allowed to flow from an orifice over the surface of the article, the excess which drains off being returned to the containing vessel.

Another process of metal covering is intermediate between the use of solutions and the use of solid celluloid coverings. The lacquer or enamel is made in such a high concentration as to be a plastic semi-solid. This is applied to the article sometimes by mechanical means, sometimes by hand with a palette knife, and after the coating has partly dried it is moulded to the desired shape in a specially designed press.

Coatings for metals may be classified as follows :—

(1) Transparent lacquers, either colourless or coloured.
(2) Enamels, white, black or coloured.
(3) Metal-powder coatings, such as bronze or aluminium paints.

These usually contain resins in addition to the nitrocellulose. The resins add body to the solution, and promote adhesion.

Transparent Lacquers.

Gardner quotes as a typical solvent mixture :—

Butyl acetate	20%
Ethyl acetate	50%
Benzene	30%

to a gallon of which would be added 6 to 8 oz. of nitrocellulose (viscosity not specified). It will be noted that this formula contains no alcohol, and would have to be made up from stove-dried nitrocellulose. As it stands, it contains the solvents butyl and ethyl acetate in a sufficient proportion to ensure that they will be in excess of the non-solvent benzene at all stages of the evaporation. If nitrocellulose dehydrated with alcohol were employed, as is usual, the 8 oz. of nitrocellulose would introduce about 4 oz. of alcohol, which would not alter the properties of the lacquer appreciably. In fact, half of the benzene in the above formula might be replaced by alcohol. For use as a protective coating, Gardner recommends the introduction of 5–7% of castor oil or treated tung oil, giving a more " elastic " film. The term elastic is here used in its popular sense of " extensible." The film is actually softer

and more plastic, and less likely to strip away from the metal by shrinkage.

Wiesel suggests the following as a typical lacquer for highly polished surfaces :—

Nitrocellulose (4 sec.)	5% by weight
Alcohol	20
Benzol	20
Butyl acetate	40
Butyl alcohol	10
Ethyl acetate	4·5
Castor oil	0·5

Here the viscosity of the nitrocellulose is indicated by the expression " 4 sec." This expresses the result of an empirical test of viscosity carried out by timing the fall of a steel ball of fixed weight through a distance of 10 inches in a solution of fixed concentration in a given solvent mixture. Such a test is quite definite as long as the conditions are observed, but there is much to be said for expressing the results in recognised scientific units.

In this formula alcohol is present to the extent of 20%, so that the solution could be readily made up from nitro-cotton dehydrated in the usual way with alcohol. The precipitating tendency of benzol is amply safeguarded by the presence of alcohol, with which it forms a solvent mixture, and by the combined solvent power of the ethyl and butyl acetates. The butyl alcohol helps to slow the rate of evaporation, and assists the solvent power of the acetate. Also, like the ethyl alcohol, it forms a weak solvent mixture with the benzol. The mutual influences on solubility of the ingredients in this mixture are thus somewhat complicated.

If either of these formulæ were required for a colourless lacquer, attention would have to be paid to the colour of all the ingredients and of the original nitrocellulose. Either could be transformed into a coloured lacquer by dissolving in the liquid solvent the appropriate spirit-soluble aniline dye, or mixture of dyes. These lacquers are largely used in the fancy metal-ware industry, both for protection from corrosion and for decoration.

Enamels.

Similar formulæ with the addition of the requisite pigments and resins give the enamels. The pigments should be ground up either in the castor oil or in the plastic mass formed when the nitrocellulose is gelatinised with part of the solvent.

Enamels of this kind are used as waterproof paints on domestic metal-work, and on small articles such as motor-car accessories, scientific instruments, and sanitary goods. When the best results are required, it is usual to apply two or three coats, and to buff or rub down with fine glass-paper between the coats. The best effect of all is produced by giving a final dip or spray with a transparent celluloid lacquer, which gives a beautiful gloss to the surface.

A matt surface is obtained by increasing the quantity of pigment and/or varying the proportion of resins. This type of surface appears to be due to the pigment particles not being completely surrounded by an envelope of the nitrocellulose, as they are in a glossy enamel. It is a somewhat uncertain process in practice, as a matt enamel may under some conditions of temperature and humidity dry brighter or duller than usual. A good matt enamel should not give up colour when rubbed with the finger.

Aluminium and Bronze Mediums.

These invariably contain resins in addition to the nitrocellulose, and they are applied to metal as much for protection as for decoration. The metal powders must be very fine, so as not to clog the jet in spraying work.

When bronze powders are worked into nitrocellulose solutions it is sometimes noticed that after a few hours or days a green colour develops and the nitrocellulose begins to separate out in large clots. This is usually attributed to instability of the nitrocellulose, but it sometimes occurs with nitrocelluloses of proved stability, and when the solvents are apparently in good order. It is a phenomenon which requires investigation. It is better not to stock these solutions made up ready for use, but to work in the metal powder immediately before the paint is required. These paints are frequently applied with a brush, and have been used to a larger extent on outside work than any other nitrocellulose solution previous to the new motor-car finishes.

Motor-car Enamels.

The use of nitrocellulose enamels for covering the bodies of motor-cars has been developed chiefly in the United States, and is competing with the existing methods, which are classified by Mougey [10] as follows :—

(1) Methods employing oil and resin varnishes, applied in a similar way to coach-builders' varnishes. The applications

may consist of one priming coat, any number up to seven surfacing coats, from one to five colour coats and a glossy finishing coat.

(2) The use of stoving enamels, which require heating after application to temperatures varying from 60° to 200°. These may be applied in three coats, a primer, a colour coat and a finish. Black enamels containing bitumen are the commonest of the stoving enamels.

Both of these methods may give excellent results, but they have certain drawbacks. Varnishing in accordance with the first method is costly in time and labour. The coats take several hours to dry, and there is a considerable amount of rubbing down to be done if the best results are required. As many as twenty-eight days might be required for the complete operation.

Stoving enamels give a hard coating with a high lustre. Both processes, however, yield a coating which may have poor resistance to atmospheric conditions. The varnish coatings may develop large cracks, and the stove enamels, though more durable, sometimes become covered with a vast number of very small intersecting cracks. Both finishes are easily scratched, and a varnish finish is sensitive to petrol, oils and tar.

By the use of nitrocellulose enamels it is claimed that a finish may be obtained which is equal to that of the black stoved enamel, but without the need for stoving. Practically any colour can be obtained, and the solution can be applied by an air-spray. Compared with the first method, the number of coats can be considerably reduced, since an enamel of high nitrocellulose content is used, giving a thick coating which is dry in a very few minutes, and which can be polished to any desired degree.

According to Flaherty,[11] nitrocellulose enamels were first used on motor-cars in some of the re-finishing shops in California, but at that time the amount of nitrocellulose in the solution was so small that several coats had to be used to give sufficient thickness of film and depth of colour. The process was therefore very expensive and not adapted to general use.

The later development in motor-car enamels has been brought about entirely by the discovery of a method of producing stable nitrocelluloses of much lower viscosity than was formerly thought possible, so that the manufacturer can obtain a much higher solid content without making the enamel too viscous to spray.

The coatings obtained by the new process are said to be more

stable than those made from oil/resin paints and varnishes, and to possess better resistance to tar and petrol. They can be cleaned down with a wet mop without becoming scratched, and although the original gloss is not so good as that obtained by the best coach-builders' varnish or stoved black enamel, it can be brought up by rubbing and improves with age. The extra resisting power of nitrocellulose coatings is chiefly due to the fact mentioned in the first chapter, that the polymerisation of a drying-oil takes place slowly *after* the application of the varnish, whereas the nitrocellulose enamels already contain the polymerised base in the form of the cellulose ester.

The saving in time is remarkable. Kirkpatrick states that the time required to finish the body of one particular make of car has been reduced from 336 hours to 13½. The number of operations has been reduced by one-third, and the number of bodies in process at one time has been reduced from 2,400 to 600. Condé [18] states that the same firm were able to reduce the area of floor space given up to painting operations by 30,000 sq. feet, which in itself represented a large capital saving.

The method of manufacture of low viscosity nitrocellulose enamels follows the ordinary procedure so far as details have been published, but the precise way in which the viscosity is kept so low has been kept secret. The solvents employed are said to be chosen from amyl, butyl and ethyl acetates, amyl and butyl alcohols, xylene, toluene, benzene, ethyl alcohol and acetone, while among the gums mentioned in this connexion are shellac, soft copals and dammar.

The method of application of the enamels has been described by Flaherty.[11] Any previous coating of varnish or paint must be removed, *e.g.*, by use of the blow lamp, as the nitrocellulose solvents are liable to form soft spots over places where the previous varnish coat is not completely oxidised. When thoroughly cleaned, the metal is coated with an ordinary oxide primer, which must be allowed to oxidise fully before the enamel is sprayed on. The nitrocellulose enamel is then applied.

Respirators are worn by the workmen while they are spraying, and in British practice the car body stands in front of a concave metal shield with an extraction fan in the centre designed to withdraw the fumes. As a rule, a fairly high air pressure is used, sometimes as much as 80 lb. per square inch, but custom varies considerably in this respect.

The use of a glossy oil-resin varnish over the nitrocellulose

enamel is not recommended, as if a high gloss is required it may be obtained by friction.

Failure of the enamels in service may be due to any one of four causes: (1) Improper preparation and oxidation of the under coats. (2) Too heavy a coating of enamel. (3) Spraying the enamel too dry, either through using too high a pressure, or keeping at too great a distance from the work. (4) Allowing the enamel to settle out in the container, for want of stirring.

Imitation Leather.

The imitation leather industry originated in the process of Wilson and Story (1884), who coated cloth with a solution of nitrocellulose in a mixture of amyl acetate and castor oil.[12] The later developments have been chiefly in the use of more economical solvent mixtures, and more suitable varieties of nitrocellulose.

The fabric coated is usually cotton, commonly a canvas duck, which should be free from weaving defects giving an irregular surface, such as irregularity in the thickness of the thread. Light fabrics are usually given a dressing to weight them. Heavy fabrics are lightly fluffed so as to assist adhesion.

The solutions are applied to the moving fabric through an adjustable slot set to deliver the correct amount. The solvents chiefly used are acetone oil and ethyl acetate, diluted with alcohol, benzene and petroleum spirit. Oil must be added to ensure pliability of the coating. Castor oil is still the best, on account of its light colour and non-drying properties. It is said that blown linseed oil, colza oil and cotton-seed oil are also used, but they are liable to turn acid. The pigments are ground in the oil before introducing them into the solution. Resins are not employed.

The number of coatings may vary from three to thirty, according to the thickness of material desired, but it is likely that the advent of nitrocellulose of lower viscosity will reduce the number required for thick material. The first coatings usually contain only a small quantity of oil, as they are required primarily to secure adhesion. The intermediate layers, which give body, contain more oil, and the final coatings, which give the gloss, contain neither oil nor pigment. The cloth must be dried between the applications.

Tucker [14] discusses the question of viscosity. If this is expressed by the time taken for a steel ball, 5/16 inch in diameter, to fall through a distance of 10 inches in a solution made up from 16 oz. of nitrocellulose to 1 (U.S.) gallon of solvent, 70% ethyl acetate and 30% benzene, the viscosity of the nitrocellulose used for artificial

leather is usually a 20-second cotton. When this is made up into the correct formula, including the diluents, the viscosity is about 40 seconds.

Deschiens [15] has described the preparation of artificial leather from cellulose acetate, but the higher cost of this ester limits its employment for this purpose. It could only compete if there were special reasons for producing a material less inflammable than the nitrocellulose leather.

The imitation of the grain of real leather is put on by passing the coated cloth through engraved rollers under pressure, and sometimes the cloth is then rubbed by hand with a pad soaked in solvent containing a slightly darker pigment than that used in the coating solution. This pigment collects in the channels of the grain and produces an imitation of old leather.

Leather Dressing.

Nitrocellulose solutions are used to impart a high gloss in the so-called patent or enamelled leathers.

Patent Kid.

The processes used in making this material are described by Crockett.[16] Three coats of linseed oil varnish are usually applied, and the skins are stoved between the applications. A nitrocellulose solution is sometimes used instead of the first coat or "daub," and is said to be a 3% solution in amyl acetate. The viscosity is not specified, but it must not be too low, or the solution will penetrate the leather too much and harden it. The daub is applied by means of a brush on the grain (outer) side of the leather, which has been previously cleaned with petroleum spirit to remove grease. The other two coats are applied above the nitrocellulose coat. They consist of linseed oil, blue and black pigments, and driers, boiled for several hours at 500° F.

Patent and Enamelled Leathers.

These are now frequently prepared entirely with nitrocellulose solutions, the older linseed oil varnishes having been largely superseded. The leather should be thoroughly cleansed from grease, and quite dry. Three coats are applied, the first by means of a stiff brush, with which the solution is worked well into the leather. The second coat is applied by means of a woollen sheep-skin swab, made by tacking to a wooden handle a piece of sheepskin tanned with the wool on. The third coat is applied in the same way as

the second, and must be applied thinly and evenly. Between the applications the skins are dried at 65–100° F.

According to Clément and Rivière,[2] the solvents employed in the first coat are :—

Amyl acetate	. . . .	1800 parts
Petroleum spirit	. . . .	900 ,,
Castor oil or Boiled linseed oil	. . .	900 ,,

The second coat contains less oil and the third none, so that a high gloss is obtained.

The colour is usually a soluble (aniline) black. The leather may be embossed under a hydraulic press in order to give it any desired configuration.

Motor-car Upholstery Leather.

Herrmann and Radel [17] describe the treatment of this material in an article very fully illustrated by reproductions of photographs. The split hides are doped with nitrocellulose varnish. In this process the skins are stretched out on tables, and the first coat is put on with the same type of brush as that used by bootblacks. The later coats are applied with brushes made of Chinese hog bristle, six or seven inches long, having a wooden peg or "dutchman" in the middle so as to allow an extra quantity of material to be carried and to give a spread to the brush. It is stated that this spread is essential to produce a good finish.

The leather is sometimes finished with nitrocellulose dope alone, sometimes entirely with a japanning finish of boiled linseed oil, turpentine, naphtha, driers and pigments, and sometimes with a combination finish consisting of undercoats of nitrocellulose and finishing coats of a linseed oil japan.

Wood Coatings.

The use of nitrocellulose varnishes for the protection and decoration of wood at first sight presents a great advantage over French polishing in the great saving in time involved. Up to the present, however, there has not been great development in this direction. This may be partly due, as Clément and Rivière suggest, to the conservatism of the skilled French polisher, which is not unnatural in view of the excellent work which he turns out. Probably the

chief obstacle, however, has been the large consumption of solvent in the process, due to the absorption of the solution by the wood, and the first problem is undoubtedly to find a cheap coating to act as filler and primer. This is made possible by the use of modern low viscosity varnishes, which deposit much more solid content for the same expenditure of solvent.[18] It is sometimes advantageous to begin by rubbing in a pigment of appropriate colour damped with methylated spirit, *e.g.*, for a light coloured wood such as sycamore, plaster of Paris, finely-divided silica, chalk, or starch. Spirit varnishes (resins) may also be used as first coats, but the final effect is not usually so good.

Wood covered with a thick coating of white nitrocellulose paint is much used for sanitary purposes, and for bathroom, surgery and hospital shelves. This is given a succession of applications, allowing a few hours for drying between each, and with frequent rubbing down with glass paper to ensure smoothness. The final coats should be given with an enamel of the purest white obtainable, and sometimes a transparent coating is applied last of all to give a high gloss. Wood so treated is proof against damp and can be washed down without taking harm.

Picture frames and other decorative articles in wood are frequently coated with bronze or aluminium paints. Matt black varnishes are employed for the interior of cameras and other optical instruments.

Paper Coatings.

Paper is sometimes coated with nitrocellulose varnish either for protective purposes or for decoration. Cardboard price labels for use in retail shops are frequently coated with a transparent solution drying with a high gloss. Cheap fancy articles may be made by coating stout paper in much the same way as in the manufacture of imitation leather, using a solution containing castor oil as softener, and soluble colours of pigments. The paper may then be embossed with any desired pattern by passing it through engraved rollers.

Photographic papers are sometimes enamelled by coating with a transparent nitrocellulose varnish. Posters and time tables may be similarly treated to protect them against the weather.

Preservation of Antiques.

Solutions of cellulose acetate and cellulose nitrate have been largely used by Lucas [19] for the preservation of antiques from the recently opened Egyptian tombs. For this purpose he employed

either ordinary celluloid dissolved in acetone, amyl acetate, or a mixture of the two; or cellulose acetate in acetone. No mention is made of any special precautions taken to ensure the stability of the cellulose ester base, a matter which should not be overlooked when treating valuable specimens.

These solutions were employed for all kinds of materials—faience, glass, inlaid work, pottery, stone, wood, alabaster, amber and ivory. They were usually applied by means of a small camel's-hair brush or a piece of pointed wood. Porous materials, such as faience or pottery, need thorough soaking with the solution at the broken edges before making the joint. Fabrics showing signs of disintegration were sprayed with the solution.

For details of the procedure the original must be consulted. There is a curious fact noted on p. 76 that silver articles sometimes absorbed a large amount of the solution.

Miscellaneous Applications.

There are a large number of miscellaneous applications of cellulose ester solutions which need not be entered into in detail since the principles involved are the same as in the applications already described.

Cement Floors.

Gardner finds that nitrocellulose lacquers form good priming coats for certain types of cement floors which have to be painted. By using them, waterproofing greases or other materials which may be in the cement are insulated from action on the enamels subsequently applied.

Imitation of Snakeskin.

Under certain conditions of evaporation, depending partly on the solvent mixture, the film left by varnishes breaks up into small irregular polygonal areas on drying. Clément and Rivière have utilised this property in an ingenious way by applying such a varnish over a coloured base and obtaining an imitation of snake's skin. A similar effect can be obtained on penholders, pencils, cartons, etc., and can be made permanent by application of a transparent coating.[2]

Crêpe Stiffeners.

Crêpe is stiffened by the application of a nitrocellulose varnish containing resins and black pigment. The varnish must give a dull, matt effect, but it must not give up pigment when rubbed or crushed.

Hats.

Hats are stiffened with a nitrocellulose or resin solution, which gives a waterproof stiffening. Straw hats are sometimes waterproofed with a nitrocellulose solution, but without resin, which would darken the colour.

Incandescent Mantles.

These are strengthened for transport by coating them with nitrocellulose slightly softened with castor oil. A high viscosity nitrocellulose is needed for this purpose so as to fill the mesh in the fabric.

Glass.

Glass may be coloured by coating it with transparent solutions coloured with various dyes, and this method is used for coating incandescent electric bulbs, street lamps and photographic lamps. A frosted appearance may be obtained by the incorporation of certain resins.

Very dilute solutions of either cellulose nitrate or acetate may be made which leave a film so thin that it shows interference colours. Such films are, however, very fragile, and it is difficult to protect them without destroying them.

Compressed Cork.

Slabs of compressed cork used as bath-room mats and floor coverings are made by incorporating cork dust with a nitrocellulose solution and pressing the product in moulds into the required shape.

Gilding Celluloid.

Transparent celluloid may be gilded on one side by spraying with a solution containing fine bronze powder. Such material is used very effectively in the button trade.

Imitation Gold Leaf.

A similar solution sprayed on to glass and stripped forms a cheap substitute for gold leaf, and is largely employed in the bookbinding trade.

Collodions.

The term collodion is usually, though not invariably, applied to solutions of cellulose nitrate in a mixture composed mainly of ether and alcohol. Several types of collodion occur in the pharmacopœias, of which the following may be quoted :—

Collodion (official) B.P. synonym Contractile Collodion.

Pyroxylin	1 part
Alcohol (90%)	12 parts
Ether (sp. gr. 0·735)	36 ,,

Acetone may be used instead of ether–alcohol, but the film obtained is opaque.

The United States Pharmacopœia formula is :—

Pyroxylin	4 parts
Ether	75 ,,
Alcohol	25 ,,

Note that the B.P. preparation is about 2% and the U.S.P. 4%.

The B.P. Codex has the following :—

Collodium Acetonum.

Pyroxylin	5 parts
Clove Oil	2 ,,
Amyl Acetate	25 ,,
Benzol	20 ,,
Acetone to	100 ,,

This dries more slowly than an ether–alcohol collodion, owing to the presence of amyl acetate.

Martindale and Westcott speak highly of their "Collodium Aceto-Aethericum," which is a 5% solution of pyroxylin in ethyl acetate.

Collodium Flexile (official).

This preparation is made to yield a flexible film, instead of the "contractile" film of the above-quoted official formula, by the incorporation of castor oil :—

Contractile collodion	48 parts
Canada turpentine	2 ,,
Castor oil (by weight)	1 part

Various other formulæ are given in the Extra Pharmacopœia.

Celloidin.

This is a form of nitrocellulose prepared by the clarification and evaporation of an ether–alcohol solution. It dissolves again in ether–alcohol, yielding a solution of high transparency which is used as an embedding agent in microscopy, and also in surgery. It usually occurs in the form of small irregular cubes or flakes.

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Additional Reference.

The British Engineering Standards Association publish a pamphlet entitled "British Standards of Reference for Aircraft Dope and Protecting Covering," which includes specifications for each ingredient and method of application. To be obtained from the Secretary, 28 Victoria Street, London, S.W. 1, price 1*s.* 2*d.*, post free.

CHAPTER IX

MISCELLANEOUS

Precautions Necessary in using Cellulose Ester Varnishes—Safety Precautions—Cause of Blooming—Humidity of Atmosphere—Measurement of Humidity—Effect of Raising or Lowering Temperature—Settling of Pigments—Cleanliness of the Work—Evaporation Losses—Analysis of Cellulose Nitrate Solutions; Odour, Total Solids, Nitrogen Determinations—Precipitation of Nitrocellulose with Fusel Oil (Lorenz)—Precipitation of Nitrocellulose with Chloroform (Conley)—Precipitation of Nitrocellulose with Aqueous Electrolytes—Identification of Solvents—Viscosity—Analysis of Cellulose Acetate Varnishes—Solvent Recovery—Scientific Application of Cellulose Ester Solutions—Collodion Membranes—Interference Colours of Thin Films—Dimensions of Thinnest Obtainable Films—Density of Thin Films—Chromatic Emulsions—Transport of Cellulose Ester Solutions on British Railways.

Precautions Necessary in using Cellulose Ester Varnishes.

THESE may be classified under two headings :—

(1) Precautions necessary for the safety and comfort of the workers.

(2) Precautions required in order to get the best results.

(1) The chief precautions to be taken in the employment of cellulose ester varnishes are those required against fire. It is an essential feature of these varnishes that they dry quickly, and that being so, the air must rapidly become laden with the inflammable vapour of the solvents unless special arrangements are made to renew it. When shops are being specially constructed for industries using these solutions, it is a comparatively simple matter to plan the arrangements so that fans may draw the vapours away from the workpeople. All the vapours are heavier than air, so that a fan is most efficient when placed near the ground. Direct-coupled motor-driven fans are not advisable on account of the risk of sparking, particularly if running on direct current. A belt drive is to be preferred.

No general rule can be laid down as to the rate at which the air ought to be changed. This is governed more by the nature of the solvents than by the actual fire danger. In the aeroplane doping sheds during the war, the air was changed every two minutes, *i.e.*, the total amount of air moved by the fans in two minutes was equal to the cubic capacity of the shop.[1] This is perhaps the maximum requirement in ventilation, and it was brought about by earlier fatalities and illness caused by the poisonous vapour of tetrachlorethane. None of the solvents now in general use is as dangerous. Those of high vapour pressure, such as acetone, benzene and alcohol, require watching most closely, since the concentration of vapour which can be reached is naturally higher. Of these, benzene is most likely to give trouble, but with good ventilation it

can be used with perfect safety. It may be remarked that if the ventilation is sufficiently good to prevent any feeling of discomfort to those working in the shop, the fire danger due to the accumulation of vapour is also non-existent, provided that the extraction fans are placed low. If the fans are placed too high, there is always a risk of accumulation of heavy vapours near the floor.

Extraction fans (vacuum system) are to be preferred to fans blowing fresh air into the shop (plenum system).

When much spraying work is done, it is advisable for the operatives to wear respirators, since the dried spray contains particles of the solid contents of the lacquers, in a very fine state of division.

(2) The chief cause of failure met with in the use of cellulose ester varnishes is " blooming." This term is applied to the whitish deposit which sometimes appears on the surface of the work during drying. It is usually accompanied by brittleness of the coating, and when it occurs with white solutions, on which the milkiness does not show, it is sometimes called " chalkiness." Another way in which the same fault may be manifested is by pitting of the coating.

These faults are all due to the deposition of atmospheric moisture on the film during drying. If a thermometer, preferably one with a long bulb, is plunged into a nitrocellulose solution and withdrawn, it will be noticed that the mercury immediately begins to drop, and may fall as low as 10–15° below the temperature of the surrounding atmosphere. As a rule, before it has ceased to fall, beads of moisture will be seen on the film as it dries on the bulb. In fact, this rough test will, in the hands of an observant foreman, give useful information about atmospheric conditions. The cooling is due to the rapid evaporation of the volatile solvents, and the deposition of moisture to the fact that air of our climate always contains moisture, and that it does not hold so much when it is cold as when it is warm. Scientific readers must pardon the writer if he discusses this question in a very elementary way, as it is frequently a source of perplexity to the users of cellulose ester varnishes.

The simplest way in which to approach the subject of water vapour in the atmosphere is to consider the analogy with an aqueous solution of a crystalline salt, say potassium nitrate. The following table shows how much potassium nitrate will dissolve in 100 lb. of water at $t°$:—

$t°$	*Lb. of Potassium Nitrate*
10°	21
20°	31
30°	45
40°	64
50°	86

In a similar way, we may tabulate the weight of water vapour which will saturate 100 lb. of air at $t°$ and normal atmospheric pressure [2] :—

$t°$	*Lb. of Water Vapour*
10°	0·77
20°	1·48
30°	2·75
40°	4·89
50°	8·68

If we take a solution saturated with potassium nitrate at 40°, we see from the first table that it will contain 64 lb. of potassium nitrate to every 100 lb. of water. If we allow the temperature to fall to 30°, we see that 100 lb. of water can then only hold 45 lb. of potassium nitrate, so that 19 lb. of the salt must be deposited from the solution in the solid form.

Similarly, if we have the air of a room saturated with water vapour at 40°, we see from the second table that it will contain 4·89 lb. of water vapour for every 100 lb. of air. If we allow the temperature to fall to 30°, we see that 100 lb. of air can then only hold 2·75 lb. of water vapour, and the remainder, 2·14 lb. must be deposited. This moisture separates in fact as a dew or fog.

Conversely, if we warm up a solution of potassium nitrate, saturated at 30°, from 30° to 40°, we can dissolve in it an additional 19 lb. of potassium nitrate for every 100 lb. of water present. Similarly, if we warm up the air of a room, which is saturated with moisture at 30°, from 30° to 40°, we can make it take up an additional 2·14 lb. of water vapour for every 100 lb. of dry air present.

The fact expressed in the last sentence is the source of the misapprehension so often encountered, that "warming the air dries it." It does not. Warming the air enables it to take up an additional quantity of water vapour *if it is maintained at the higher temperature*, but if it is allowed to fall in temperature to its original state, all this extra water vapour must be deposited again. For example, it is of no use to draw air over steam pipes by means of a fan and deliver it into a cold shop. Steam pipes *inside the shop* are useful if great care is taken that all the joints are sound. A small leak of steam will speedily saturate the air of a room with moisture. Steam pipes outside the shop are only useful if the volume of air delivered over them, and the heat supplied to the air, are sufficient to warm the whole atmosphere of the shop.

The outer atmosphere is not often entirely saturated with moisture. What is usually called the "*humidity*" is the proportion (expressed as a percentage) between the amount of water vapour

actually present and the amount that would be present if the air were saturated with it. If, for example, 100 lb. of air at a certain temperature contains 1 lb. of water vapour, but is capable of holding 1·5 lb., its humidity is

$$\frac{1{\cdot}0}{1{\cdot}5} \times 100 = 66{\cdot}7\%.$$

The difference between humidity and 100%, therefore, expresses the drying power of the air at its existing temperature.

Since the atmosphere always contains moisture, it is always possible, by reducing the temperature sufficiently, to reach a point at which it is saturated, *i.e.*, at which dew begins to deposit. This temperature is known as the *dew point*. Returning to our original experiment with the thermometer dipped into a nitrocellulose solution and then withdrawn, we see that the appearance of the beads of moisture on the film is due to the fact that the film has cooled (by evaporation of the solvent) below the dew point of the atmosphere.

Measurements of humidity and dew point are useful data for those continuously employing cellulose ester solutions. They can be simply determined by means of an apparatus known as the "wet and dry bulb thermometer," which consists of two identical thermometers mounted side by side on the same stand. One of the bulbs—the "wet bulb"—is covered with a piece of muslin, which is connected by a few strands of cotton to a small reservoir containing water. The capillary action of the cotton keeps the muslin continually damp with water. When the air is very dry, the moisture evaporates rapidly from the muslin, and lowers the temperature of the mercury. If the air is damp, evaporation of the water is hindered, and the lowering of temperature is less. Hence the difference between the temperatures recorded by the two thermometers is governed by and measures the humidity of the surrounding air. Tables, originally complied by Glaisher,[3] are available from which the humidity of the air can be read directly from the temperatures of the wet bulb and the dry bulb.

A modern variation of the wet and dry bulb thermometer is made in which the thermometers can be whirled on an axle, so that the air is in rapid motion past the bulbs. Instruments known as hygrometers are also made which indicate the humidity directly on a dial. They depend on the influence of atmospheric moisture on the length of animal fibres such as horse-hair.

The following monthly averages of atmospheric temperature (dry bulb), wet bulb temperature, humidity and dew point may be

of interest. They were taken outside the writer's laboratory (Suffolk) at mid-day on working days, and show the kind of variation which occurs between summer and winter weather :—

1924.	Dry bulb.	Wet bulb.	Dew point.	Humidity %.
July	68·4° F.	63·3° F.	60·0° F.	75·6
August	65·3	58·3	52·6	64·2
September	63·3	57·3	52·2	67·4
October	57·2	53·2	49·4	74·7
November	50·6	46·7	42·5	75·2
December	47·8	44·6	40·7	76·8

The chief point to observe is that the dew point in the open air is lower in winter than in summer, and this is the temperature at which the atmosphere begins to deposit dew. Supposing that, *without any change in the actual weight of the water vapour content*, the air defined in the above table were drawn into a shop at a temperature of 55° F. The dew point in July averaged 60° F.; therefore this air at 55° F. would be below its dew point and would become foggy and deposit dew. The other five samples would remain clear.

The usual working temperature of a shop is about 65° F., and this is a fairer temperature to take. If the above six samples of air were drawn, without change of water content, into a shop at 65° F., what effect would it have on their drying properties? This can easily be ascertained from Glaisher's tables. Since the water content has not changed, the dew point of each sample must be unchanged also. We have to find therefore what would be the humidity of six samples of air, whose dry bulb temperature was in each case 65° F., but whose dew points were 60·0, 52·6, 52·2, 49·4, 42·5 and 40·7 respectively. The answers are given in the following table :—

1924.	Humidity if at 65° F.
July	84%
August	64
September	63
October	57
November	44
December	41

It will be noticed that the humidity of the July air has been increased, that of August has hardly changed, while the average air of the other four months has all been reduced in humidity by bringing it

to the uniform temperature of 65° F. The content of water vapour has not been altered. The change has occurred in the proportion between the actual water content, and the water that the air could hold if saturated; in other words, the drying power of the air has been changed, although its water content has not.

It follows from this that if work is carried on in a shop maintained at a uniform temperature throughout the year, trouble with blooming is more likely to occur in summer, when the dew point of the outer air is high, than in winter, when it is low. In practice, conditions are not quite so simple as they have been assumed to be in this example. For example, the presence of human beings in a room alters the humidity conditions, owing to the moisture in expired air; but the main conclusions hold.

Solutions sold by manufacturers as drying bright contain sufficient high boiling solvent to prevent blooming under all usual atmospheric conditions, but when consumers ask for specially quick-drying solutions, blooming becomes a frequent problem.

It is evident that there are three ways of preventing the deposition of atmospheric moisture on the film :—

(1) Drying the air which is being drawn into the shop by the exhaust fans.

(2) Checking the rate of evaporation, so as to diminish the cooling of the film.

(3) Carrying out the drying operation in a chamber at a slightly higher temperature than the work-room.

A combination of (2) and (3) is the usual remedy for blooming. Drying the air, the first remedy, is a rather more complicated process than most solution-users care to undertake. It may be carried out by passing the incoming air over refrigerating coils, when the moisture in the air is deposited on the pipes as ice, or by drawing the air through a drying tower fed with sulphuric acid. Sometimes trays of calcium chloride in lumps are placed in the drying chamber, thereby combining methods (1) and (3). If the work, after having been sprayed or dipped, is promptly transferred to a warm compartment, at a temperature of 80° to 90° F., solutions made with ordinarily volatile solvents will usually dry bright. In such a compartment, the rate of evaporation can be checked by means of ventilators, thus applying method (2). The air under these conditions becomes highly charged with vapour, and precautions against fire must be rigorously enforced.

Varnishes containing high-boiling solvents do not often give trouble through blooming, but it must be remembered that the

high-boiling solvents are the expensive ones, and keen competition will compel manufacturers to reduce the percentage of these solvents to the lowest limit.

Settling.—The rate of settling of the pigment in a well-made cellulose ester varnish is extremely slow, but nevertheless it does occur when the pigment is heavy or present in large amount. Such varnishes should therefore be well stirred before use, and should not be stocked for long, if this can be avoided. If the varnish is allowed to settle, the top layers will be deficient in covering power, and the bottom layer will give brittle or rough coatings.

Cleanliness.—It is particularly necessary that surfaces, especially metallic surfaces, to be coated with either a cellulose nitrate or cellulose acetate varnish, should be quite clean. Grease or oil is specially to be avoided, as it prevents proper adhesion. Washing the surface with petroleum spirit, benzol or toluol is recommended when practicable, but the surface must be quite dry again before the first coating is applied.

Evaporation Losses.—It is the custom in many factories using cellulose ester solutions to distribute the solutions about the shops in small vessels or containers, for the convenience of the work-people. Unless these can be closed at night with an air-tight cover, they should always be emptied back into the main storage vessel. Otherwise a great deal of solvent is wasted, some of the varnish is spoilt, the air of the shop is needlessly contaminated with solvent vapours and the fire risk while the shop is unoccupied is unnecessarily increased.

Analysis of Cellulose Nitrate Varnishes.—In view of the fact that very few of the ingredients of cellulose ester varnishes are, or even approximate to, chemically pure substances, it is evident that the deduction of a formula by the analysis of a sample is always a matter of great difficulty, and sometimes an impossibility. In fact, as a rule more can be learned about a sample in a short time by close observations of its behaviour on filming, its odour and its price, than can be learned in the same time from its chemical behaviour.

Certain methods are available, however, and yield results which are of considerable assistance.

(1) *Odour.*—The constituents of the solvent can often be identified by the smell of the sample. Amyl acetate is unmistakable, but may mask butyl acetate. Acetone, benzene, wood spirit and ethyl acetate can usually be recognised, even when present together. Petroleum spirit is less easily distinguished and ethyl alcohol is difficult to detect. There are, of course, considerable personal

differences in the acuteness of the sense of smell and the power of distinguishing the constituents of mixtures.

(2) *Total Solids.*—The percentage of total solids is determined by the evaporation of a small weighed quantity to constant weight. The solution should be spread out in as thin a film as possible. Conley [5] recommends using just enough of the solution to cover the bottom of the weighing bottle, but this limits the quantity rather stringently. On the other hand, weighing on a clock glass is inadmissible on account of the rapid loss of solvent during weighing. A preferable method is to weigh the sample in a wide-mouthed bottle or sample tin; the rounded bottom of a stout weighed glass tube is then dipped into the solution and withdrawn, rotating it in the fingers if there is a tendency to drip. The sample is weighed again, and the difference in weight is the amount transferred to the outside of the tube. The latter is kept in a warm place until free from the smell of solvent and is then weighed at intervals until of sufficiently constant weight. The appearance and manner of drying of the film can be very conveniently studied in this way, and the coating is easily removed as a thimble by putting the tube in hot water for a few seconds.

Nitrogen Determinations.—Writers on the subject do not appear to have realised the value of a nitrogen determination in a portion of the film obtained from a total solid determination of a cellulose nitrate solution. This is best carried out by the Schultze-Tiemann method on a weighed quantity of about 0·3 gramme of the sample. [It will probably be noticed that there is a distinct odour of solvent when this piece is boiled in the flask—a sign that the estimation of solid content has given a higher figure than the true one.] From the nitrogen figure it is possible to obtain immediately an approximate indication of what proportion of the solid content is *not* nitrocellulose. The nitrocelluloses used in varnish manufacture usually contain from 11·7 to 12·2% of nitrogen. Hence if the nitrogen is much lower than this, there must be an appreciable quantity of other ingredients and the percentage of nitrocellulose in the film will be roughly

$$\frac{x}{12} \times 100\%$$

of the weight of the film, x being the determined percentage of nitrogen.

If the film is transparent and nearly colourless, the other constituent may be castor oil, which imparts its characteristic odour to the film and makes it supple. If the film is transparent, somewhat

dark in colour and hard, resins are indicated. If opaque, there are probably pigments present and a determination of ash should be made to compare with the value calculated from the percentage of nitrocellulose. The ash may be analysed by the ordinary methods of inorganic analysis. The presence of oil in the film is often shown by drops floating on the surface of the liquor remaining in the flask after the completion of the nitrogen determination. Resins, oil and pigment may all be present together, or any two of them, and the problem becomes complicated. Extraction with an organic solvent which does not dissolve nitrocellulose, such as chloroform (best), benzene or petroleum spirit, will often take out the resins and/or oil, leaving pigment and nitrocellulose together. A fresh nitrogen determination at this stage will check the loss of weight of the film and the weight of the oil extracted. When weighing an oil extract which is being taken to approximately constant weight, it is usually advantageous to employ a small porcelain dish resting on a watch glass or small clock glass, so that any oil creeping over the side of the dish is not lost.

Precipitation with Fusel Oil.—For a mixture containing nitrocellulose, resin and pigment, amyl acetate, amyl alcohol, methyl alcohol and petroleum spirit, Lorenz [4] recommends a different method, which has its advantages. To 100 c.c. of the varnish are added gradually with continuous stirring 200 c.c. of fusel oil. The nitrocellulose is precipitated as a voluminous gel. Fifty c.c. of the clear liquor are drawn off and saponified with standard alcoholic potash. If the only ester present is *amyl acetate*, the amount in the 50 c.c. is one-sixth of that originally present in 100 c.c. of the varnish.

[If butyl or ethyl acetate is present as well as amyl acetate, it is only possible to obtain the total percentage of combined acetic acid in the original varnish, a figure that may be quite useful.]

The remaining 250 c.c. from the previous determination are transferred to a tared filter and washed with warm fusel oil until no more solid matter is extracted. The object of this is to extract all the resins (of which amyl alcohol is perhaps the most general solvent), leaving the nitrocellulose on the filter-paper. An aliquot portion of the filtrate is taken to dryness to give the percentage of resins. Lorenz remarks that "the nature of the gum resins and camphor which constitute the residue may be determined by the usual methods." If camphor is present, the writer would much prefer to get rid of it before weighing the resins, since the amount of camphor left after evaporating to dryness 150 c.c. of fusel oil (as Lorenz recommends) would be much less than the camphor originally

present, because of its high volatility. The writer would suggest moistening the residue of resins with toluene, and taking to dryness again, repeating this operation until sufficient constancy of weight is reached. The presence of small amounts of camphor in varnish samples is a much more awkward analytical problem than the estimation of camphor in solid celluloid. The only safe method of camphor estimation is by the polarimeter (which, of course, fails when optically inactive camphor is used), and it is not easy to get from a sample of varnish a solution of the camphor (in a pure solvent) of sufficient concentration to give an accurate polarimeter measurement of its optical activity. The writer would prefer to proceed on the following assumptions :—

(*a*) If camphor is detected qualitatively, and the nitrogen content of the nitrocellulose is not greater than 11%, the varnish has probably been made from ordinary celluloid, and should be matched by the use of ordinary celluloid based on the nitrocellulose content of the latter.

(*b*) If the nitrogen content of the nitrocellulose is about 12% and camphor is present, the varnish has probably been made from waste cinema film, and should be matched by the use of cinema film based on its nitrocellulose content.

The assumption underlying this procedure is that camphor is not likely to be added to a varnish made up from fresh nitrocellulose, and its presence usually indicates the use of a form of celluloid scrap. Admittedly exceptions occur. In any case, the proportion of camphor is not likely to exceed 25% of the weight of nitrocellulose.

Returning to the analytical scheme of Lorenz, the mass on the filter-paper now consists of nitrocellulose and adhering fusel oil, together with pigment. It is washed with a mixture of equal parts of acetone and amyl acetate, which dissolves the nitrocellulose, and the solution passing through the filter is collected. On evaporation to dryness of the whole of this (or an aliquot portion), the nitrocellulose is obtained and can be weighed. The writer's experience is that the weight of nitrocellulose so obtained is likely to be too high. (See p. 154.)

The residue on the filter-paper is the pigment, the weight of which is obtained by drying to constant weight at 100° and deducting the weight of the filter. It is the writer's opinion that with many of the finely-ground pigments used in present-day lacquers, a certain amount would pass through the filter with the nitrocellulose, so that the figure would be only approximately correct. Some method such as this, however, is the only practicable one if the pigment is

some form of carbon, since it cannot be ignited without loss. If the pigment is a permanent oxide, such as zinc oxide, it is better to determine pigment by ignition of the film obtained in the estimation of total solid contents, as already described.

Petroleum spirit is determined by adding 75 c.c. of concentrated sulphuric acid to 50 c.c. of the solution in a graduated cylinder, stirring vigorously. After several hours, the petroleum spirit, which is the only ingredient insoluble in the acid, will have risen to the top and the volume may be read.

Lorenz estimates the amounts of methyl and amyl alcohol by distilling 100 c.c. of the original sample, using a fractionating column, and assuming that the volume of distillate coming over below 75° is equal to the content of methyl alcohol. Of the four liquid constituents of the mixture, amyl acetate, amyl alcohol, methyl alcohol and petroleum spirit, three have thus been determined, and the amyl alcohol is calculated by difference.

Conley's Scheme of Analysis.—Conley [5] abandons the method of precipitation by fusel oil, since some nitrocellulose remains in solution. He prefers to measure out 10 c.c. of the solution, and precipitate by the gradual addition of chloroform, with continuous shaking. If no resins or pigments are present, the precipitate is pure nitrocellulose, and may be filtered off, dried, and weighed. If resins are present in considerable amount, the first precipitate of nitrocellulose will be contaminated with resin. It is then necessary to decant the clear liquor as completely as possible, to redissolve the nitrocellulose in the smallest possible quantity of solvent, and to reprecipitate with chloroform. Conley does not suggest a solvent for this purpose, but the writer would suggest a low-boiling solvent such as acetone, so as to diminish the risk of contaminating the final precipitate with a high-boiling solvent such as amyl acetate.

Resins or oil are estimated by evaporation to dryness of an aliquot portion of the combined filtrate. Castor oil is recognised by its smell and its relative insolubility in petroleum spirit. It is almost impossible to identify the resins obtained in this way, since their solubility is frequently altered by the treatment they have received.

The writer's experience is that no method of precipitation of nitrocellulose by organic solvents is cleanly or easy to carry out, although in view of the fact that the analysis of a nitrocellulose varnish is at best a very approximate affair, the method is probably good enough. From the researches of Knoevenagel and his collaborators on the swelling of cellulose acetate, it is probable that the precipitated nitrocellulose contains absorbed solvent, in some kind of equilibrium with the surrounding liquid, and it is difficult to

remove this in reasonable time by drying. If a precipitate so obtained, after having been taken down to approximately constant weight, is transferred to a test-tube and boiled with a little water, there is an immediate odour of solvent, showing that the nitrocellulose is not pure.

Precipitation with Aqueous Electrolytes.—The following method is much cleaner, and has been employed in the writer's laboratory for several years, if a more accurate determination is necessary. A film is first obtained directly from a weighed or measured quantity of the original solution, as in the determination of solid content. The amount of film should be enough to yield about 0·5 gramme of nitrocellulose. If oils or resins are present, they are extracted under reflux or in a Soxhlet, with chloroform or any other appropriate solvent. If they are not present, this step is unnecessary. The film is then dissolved in 50 c.c. of acetone, and diluted with aqueous alcohol (50%). The quantity cannot be stated definitely, since it differs according to the solubility of the nitrocellulose, but it must be sufficient to convert the solution to an opalescent suspensoid colloid, blue by reflected light and red by transmitted light. Such a solution would pass unchanged through filter-paper. On adding to it a dilute aqueous solution of an electrolyte, such as 2% ammonium chloride, it is coagulated to a manageable precipitate. Here also the required conditions are variable. Sometimes it is better to precipitate hot, sometimes cold. A little experience is the best guide. Under favourable conditions, the precipitate is as easy to manipulate as silver chloride. The liquid is brought to the boil, allowed to settle, and filtered off through a Gooch crucible under suction, the first few washings being decanted off. Washing is complete when the filtrate contains no chloride. The precipitate is dried in the usual way at about 40°, and when constant weight is obtained, it may be washed directly into the Schultze-Tiemann apparatus for nitrogen determination. The greater purity of the nitrocellulose so obtained is shown by the fact that it always gives a higher nitrogen content than those obtained by precipitation with an organic liquid, and the apparatus is left quite clean.

This method is a modification of one first suggested by Dubovitz,[6] who precipitates an acetone solution of nitrocellulose directly with a solution of ammonium chloride. The modification is a little more elastic, and the precipitated nitrocellulose is less likely to contain enclosed impurities. The hot aqueous solution of acetone and alcohol is very efficacious in keeping camphor and other organic solvents in solution.

Identification of the Solvents.—Conley recommends dry distillation

up to 120° of 100 c.c. of the varnish from a distilling flask heated in a paraffin bath. Above 120°, water is added, and a steam distillation is substituted. The product of dry distillation will contain all the low-boiling solvents present, *e.g.*, methyl and ethyl alcohols, acetone, methyl ethyl ketone, ethyl acetate, benzene and part of the petroleum spirit. The product of the steam distillation will contain, *e.g.*, amyl acetate, butyl acetate, higher acetone oils, and the remainder of the petroleum spirit.

The rigid separation and identification of these in the limited time available in a technical laboratory is impossible. The low-boiling solvent should be fractionated, and a selection from the following tests applied to the fractions: odour, specific gravity, miscibility with water, miscibility with salt solution, miscibility with concentrated sulphuric acid, iodoform reaction, reaction of immiscible liquids with nitric acid. The product of the steam distillation, after salting out dissolved solvents from the water layer, may be similarly treated. From the indications obtained it is usually possible after some experience to match fairly closely the composition of the solvent mixture.

Viscosity.

This is the most important property of all. It should be measured by a method giving results comparable with those of other investigators, and the writer strongly recommends the use of the falling sphere viscometer as standardised by Gibson and Jacobs.[7] The instrument should be calibrated against a standard material such as glycerine, and the result expressed either in absolute C.G.S. units, or in a unit easily convertible into the scientific unit. A modification of the falling sphere viscometer due to Mardles can be used for opaque solutions in which a weight is attached to a fine wire on the other end of which is a counterpoise.[8] The wire is hung over a low-friction pulley and the weight is allowed to fall in the solution. The rate of fall is then measured by the rate of rise of the counterpoise. The B.E.S.A. specifications favour the Ostwald viscometer. Their standardisation of the temperature of 25° for viscosity determinations is to be commended. Although this temperature is a little higher than that at which most solutions are used, it is one that can be maintained in a thermostat in hot weather without difficulty.

Analysis of Cellulose Acetate Varnishes.

There is no literature on the subject of the analysis of cellulose acetate varnishes, probably because there has been very little need

for such analyses up to the present. The writer suggests the following scheme as a working basis :—

(*a*) Determination of solid content by filming-off a weighed quantity of solution. The solid content consists of cellulose acetate and the softeners, such as triphenyl phosphate, triacetin, benzyl alcohol, acetanilide. Extraction of the film with low-boiling non-solvents such as ethyl ether. Weight of cellulose acetate remaining, and determination of acetyl group if of interest. Resins are not found in cellulose acetate varnishes.

(*b*) Identification of the softener by precipitating a larger quantity of the dope with ether, filtering off the precipitated cellulose acetate and evaporating to approximately constant weight. Test the residue for organic phosphate and for the phenyl, glyceryl, benzyl, acetyl and amino-radicals. Quantitative determination is likely to be difficult or impossible. Estimations of phosphate and of nitrogen are most likely to yield useful information.

(*c*) Dry distillation to 120° followed by steam distillation, as in Conley's scheme for nitrocellulose varnishes, should give much information about the volatile solvents. Tetrachloroethane is not likely to be found in a modern acetate varnish, but is easily recognised by the smell. The solvents for which a look-out should be kept are acetone, methyl ethyl ketone, alcohol, benzol, methyl acetate. Fractionation of the dry distillate and miscibility tests of the fractions would show the presence of benzol, acetone and methyl ethyl ketone (note smell and boiling point). Quantitative determinations are not likely to be of much use, but a saponification to determine ester (methyl acetate) and an acetylation to determine free hydroxyl (ethyl alcohol and possibly methyl alcohol) may be worth while.

Addendum to Analysis.

In converting proportions by weight to proportions by volume, or *vice versa*, it is necessary to know the specific gravity of the solution. There is no advantage to be gained by carrying out this determination in a pyknometer with the precautions usual in scientific work, and it is difficult to do so on account of the high viscosity and volatility of the solution. A better way is to weigh 25 or 50 c.c. in a tared graduated cylinder. The accuracy obtained in this way is much greater than the probable accuracy of any determinations of individual solvents which may be attempted.

The cultivation of a sense of proportion is very necessary in

technical analysis if high accuracy is unattainable, and will often lead to much saving of time. The accuracy of an analysis is limited by that of its least accurate step, and it is to the improvement of the latter that care and attention should always be given.

Solvent Recovery.

In view of the fact that a large proportion of the weight of a cellulose ester varnish consists of volatile liquids which evaporate from the coating in the course of drying, there would appear to be considerable scope for the application of processes of solvent recovery. Actually, however, there are few industries using these varnishes in which solvent recovery has been installed. Perhaps the chief reason for this is that the consumption of cellulose ester varnishes is spread over a large number of small users, and solvent recovery is much more profitable for large quantities of solvent than for small, on account of the high overhead charges on small plants. Another factor is the considerable range of different solvents employed, and the difficulty of ascertaining the exact composition of a mixed recovered solvent—knowledge which is essential before the solvent can be employed again for a similar purpose. However, very great strides were made in the theory and practice of solvent recovery during the war, and it is possible that there may be considerable developments during the next few years.

The processes of solvent recovery fall into three principal classes :—

(1) Absorption of the solvent vapour in a suitable liquid or combination of liquids.
(2) Adsorption of the solvent vapour on the surface of solids.
(3) Direct condensation of the vapours, using refrigeration.

The third method is only economical when the concentration of the vapour is very high, or in certain processes where partial vacuum is employed to hasten evaporation. Since the vapour coming from work-rooms in which cellulose ester solutions are used is necessarily dilute, this method need not be further considered.

The first method is the one which has been used to the greatest extent in industry, and usually resolves itself into a search for a suitable absorbent. When alcohol vapours alone have to be captured, as in the final stages of manufacture of certain soaps, water is an excellent absorbent. In the Chardonnet process of artificial silk manufacture, in which an ether–alcohol solution of nitrocellulose is formed into threads, large quantities of ether–alcohol

are set free, and much of the earlier work was carried out in connexion with this industry. Although water is an excellent absorbent for alcohol, it is not so for ether, and the only absorbents which were at all successful in capturing both solvents on a large scale before the war were amyl alcohol, and, better, sulphuric acid. When the manufacture of R.D.B. cordite, which used ether–alcohol in place of acetone as the solvent, was undertaken on an enormous scale in Great Britain during the war, the question of recovery became pressing, and absorption in sulphuric acid was carried on for some time at Gretna. A peculiarity of this process is that ethyl alcohol reacts with sulphuric acid to form ethyl hydrogen sulphate, which reacts reversibly with either alcohol or water to form ether or alcohol respectively, according to the equations :—

(1) $C_2H_5{\cdot}H{\cdot}SO_4 + C_2H_5{\cdot}OH \rightleftharpoons C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2SO_4$.
(2) $C_2H_5{\cdot}H{\cdot}SO_4 + H_2O \rightleftharpoons C_2H_5{\cdot}OH + H_2SO_4$.

Hence the proportions of ether and alcohol in the recovered solvent altered according to the concentration conditions when the absorbent was distilled. The equilibria in this process were studied by Masson and McEwan.[9] The disadvantage of this process was the excessive corrosion of plant brought about by the sulphuric acid.

The use of cresol as an absorbent was patented by Brégeat in 1917,[10] and this substance was found to be an excellent absorbent for both ether and alcohol. A large experimental plant working on this system was erected at Gretna, and a complete plant for dealing with the whole of the vapour from the cordite stoves was erected, but not used owing to the termination of the war. In this plant the vapours were drawn by immense fans through Whessoe scrubbers through which cresol was circulated in counter-current. The saturated cresol was steam distilled to remove the alcohol and ether, and was sent back, after being cooled, to the scrubbers. The crude distillate was distilled over soda to remove cresol and fractionated for the recovery of alcohol and ether. Some of the information obtained at Gretna in the design and working of the plants has been published in the Technical Records of the Ministry of Munitions.[11]

Since cresol is miscible in all proportions with the common cellulose ester solvents, it is probable that it would, under favourable conditions, effect a good recovery of the mixed vapours with which it would have to deal. According to Drinker,[12] methyl, ethyl and amyl alcohols and acetates, acetone, benzene, toluene, xylene and chloroform can all be recovered in satisfactory yield, but it is not stated how large a plant is necessary before a satisfactory return

on the capital outlay is assured. The rapid fluctuations in the prices of solvents since the war do not make the problem any easier.

The adsorbents used in the second method are activated charcoal and silica gel, the former, as its name implies, a specially prepared carbon, and the latter a form of precipitated silica. War-time experience with charcoal used in the box respirator as an absorbent proved the efficacy of this substance as a means of removing vapours of substances of high molecular weight from air, and its use for solvent recovery is based on this absorbent power. Silica gel possesses similar properties, and the rival claims of these two absorbents are still under discussion. Neither appears to have been used yet in this country for the recovery of solvents from varnishing operations, but each promises to be a serious rival to the processes using liquid absorbents.

Scientific Applications.

Collodion Membranes.—The properties of collodion membranes have interested scientific investigators ever since the middle of the nineteenth century, chiefly on account of their restricted permeability. There is a useful historical summary in Worden's "Nitrocellulose Industry." [13] The interest in this subject has increased rather than diminished during the last few years, owing to the prominence which the subjects of permeability and osmotic pressure have assumed in biology, medicine and chemistry. The writer is not qualified to give an extended account of this work, which would in any case be out of place in this volume, but a short reference should be made to it in so far as cellulose nitrate solutions are concerned.

Collodion membranes are made by allowing a solution of nitrocellulose in ether alcohol to evaporate, leaving a film. If, for example, a test-tube is dipped into such a solution, withdrawn and rotated, the solution rapidly thickens to a firm jelly and will in time dry up to a tenacious film. Before that stage is reached, however, the tube is dipped into water, which stiffens or "sets" the film, which can then be withdrawn from the outside of the tube as a thimble or sac. Such membranes may be made, by methods to be mentioned later, to vary considerably in permeability and can be used to filter off substances which would pass through any ordinary filtering medium such as filter-paper. To this process Bechhold applied the word "ultra-filtration." The collodion membrane may be made to withstand somewhat high pressures.

Walpole has published a considerable amount of information on this subject.[14] The use of these membranes depends on the

different porosity of the gel of the membrane to molecules of different sizes. If, instead of using the membrane as a filter, the filtrate side of the membrane is bathed in a solution other than the filtrate, the process becomes dialysis, and Walpole finds many advantages in dialysis under pressure, using collodion bags which will stand a pressure of 2—3 atmospheres. Following earlier work by Martin and Cherry, he found that the toxins of both tetanus and diphtheria were held back by collodion membranes, the filtrates or dialysates of the sera being free from them.

Walpole found that collodion membranes were more uniform than parchment, and proposed to standardise them. The properties of these films depend on a large number of factors, beginning with the origin of the cellulose and its treatment before nitration, and ending with the pressure applied to the membrane when it is in use. They can, however, be characterised by two factors :—

(1) The weight of dry nitrocellulose per square centimetre of the film.

(2) The wetness of the film, which is defined as the ratio of the wet weight of the film (after being soaked in distilled water until it is saturated) to the weight of nitrocellulose which it contains.

The wetness of the film is a measure of its porosity, and it diminishes as the time allowed for evaporation in the preparation of the membrane increases. Thus the permeability of a film which has dried up completely before it is detached from the glass support is very low.

The weakness of this method of characterisation seems to the writer to be that a film containing comparatively few large pores, and another containing comparatively many small pores, might hold the same amount of water, *i.e.*, be equally wet, and yet differ considerably in permeability. Films made from the same solution of nitrocellulose with different times of drying might give reproducible results if standardised in this way, but it seems doubtful whether the results could be repeated if the films were made from an ether–alcohol solution of an entirely different sample of nitrocellulose. However, Walpole obtained very interesting results, and gives the characteristic factors for films which would pass all simple molecules, but retain quantitatively all antigens; he also gives data on the permeability of the membranes to various enzymes.

Keeble [15] found that the hormone of the sensitive plant *Mimosa pudica*, by which the excitation of the tissue is transmitted, will diffuse across a film of collodion without losing its potency.

W. Brown [16] has studied the technique of membrane preparation. The permeability of the film may be altered by soaking it in various mixtures of water and alcohol, and Brown suggests an alcohol index, denoting the strength of alcohol with which a film comes into equilibrium. Membranes can be made that will hold back so simple a molecule as copper sulphate, or that will pass so large a molecule as aniline blue. He expresses the process of membrane formation in a generalised form. If we have a " restraining liquid " A which is not imbibed by the membrane, and a " swelling liquid " B which is strongly imbibed by the membrane, then if A and B are miscible in all proportions, it is possible to obtain grades of permeability by steeping the films in mixtures of A and B, subsequently washing them in A. The higher the proportion of B in the steeping liquid the greater the permeability obtained. In this way, Brown has prepared membranes of cellulose nitrate, cellulose acetate, agar and gelatin.

Farmer [17] also found that the permeability varied according to the time of drying, and Eggerth [18] that it depended on the proportion of alcohol in the original collodion. Gans [19] found that the permeability could be varied by the use of acetic acid. Looney [20] obtained more flexible membranes by using a proportion of ethyl acetate in the collodion, but this increased flexibility would probably not be permanent.

These researches are recalled by the work of Knoevenagel (*q.v.*) on swelling, which is directly related to them.

Wegelin [21] used solutions of nitrocellulose in acetic acid instead of ether–alcohol for the preparation of the membranes, and found that the film from a 7·5% solution was ten times as porous as a film from a 15% solution. Experimental details are given. The membranes were used for the dialytic purification of various well-known inorganic colloids, and he suggests using them for the measurement of the size of particles in colloidal solutions and for the purification of precipitates not easily washed by ordinary methods.

S. L. Bigelow [22] in 1907 studied the permeability of collodion membranes, gold-beaters' skin and parchment paper, to pure liquids, and concluded that the rate of passage of the liquids through them was governed by the same laws as the flow of liquids through capillary tubes. Duclaux and Errera [23] in 1924 found that the velocity of filtration of water, aqueous solutions and certain organic liquids through collodion membranes was approximately proportional to the viscosity, and thus support Bigelow's conclusions. Bartell and Carpenter,[24] however, found examples of anomalous osmosis, which they attributed to the influence of the electrical

properties of the membrane system. It is of interest to note that they prepared their films on the surface of mercury. Preuner and Roder [25] also found abnormal osmosis, which they explained by the existence of a potential difference between the walls of the membrane, differing according to the concentration of the solutions.

Duclaux [26] has patented the preparation of continuous lengths of membranes for ultra-filtration by spreading a solution of a cellulose ester on a moving strip of fabric and coagulating the film in a suitable liquid.

Various papers have been published during the last few years dealing with the preparation of membrane filters, and their employment in analytical operations, among which those of Zsigmondy and Bachmann,[27] Bachmann,[28] Jander,[29] Kling and Lassieur,[30] and Bechhold and Gutlohn [31] may be mentioned.

Miscellaneous Scientific Uses.

Several investigators have interested themselves in the properties of extremely thin films of collodion, but the materials used in their experiments are sometimes described somewhat vaguely. Wood [32] prepared collodion films of soap-bubble thickness by diluting "ordinary collodion" with about ten parts of ether, pouring the mixture on a glass plate and draining it off immediately. If a square is ruled on the glass with the point of a sharp knife, and the plate is lowered into water, the square piece of film may be floated off. It may be picked off the water by lowering on to it the well-greased edge of a cylindrical support such as the bottom of a cylindrical lamp glass.

The same observer noticed [33] that a thin collodion film deposited on a bright silver surface shows brilliant colours in reflected light, which, however, were not obtained if the commercial ether in the collodion were replaced by pure ether. Similar films on glass did not give the same effect. This phenomenon attracted the attention of the late Lord Rayleigh.[34]

Boys [35] used a solution of celluloid in amyl acetate to obtain permanent iridescent films. He quotes directions given by Glew. Amyl acetate is boiled for a few minutes to remove all moisture from it. It is then used to make up a solution of celluloid in the proportion of 1 gramme in 14·6 c.c. A drop of this solution is allowed to fall on the surface of clean cold water in a large basin, and the amyl acetate is allowed to evaporate. The film may be lifted from the water on a wire ring, and becomes more brilliant as it dries in the air. Glew states that the films may be thrown into

nodes and loops by sounds of short wavelength; the effects may be studied by reflecting sunlight from the film on to a sheet of white card. Whistling or singing near the film then causes a charming combination of motion and colour on the screen.

Barton and Hunt [36] describe how extremely thin films of " celluloid " were obtained at the U.S. Bureau of Standards. One gramme of celluloid was dissolved in 400 grammes of amyl acetate, and a drop was placed on the surface of clean water and allowed to evaporate. The film was transferred to glass and its thickness was found to be 30 Ångström units (3×10^{-7} cm.). Films obtained similarly from a solution of 1 gramme in 800 grammes of amyl acetate would just hold together, but films from a solution of 1 gramme in 1200 grammes of amyl acetate broke up as the amyl acetate evaporated. If the thickness of the films decreased in the same ratio as the dilution of the solution, the thickness of the films just too thin to hold together would be 10 Ångström units, and this agrees with the thickness calculated from the density of celluloid, the concentration of the solution, and the area of the film. Hence the molecular complex of celluloid is not more than 10 Ångström units ($= 10^{-7}$ cm.) in diameter.* This agrees with results of similar experiments on films of oil and other organic substances.

From the description of the material as " celluloid," the authors probably employed either ordinary celluloid or cinema film in these experiments, *i.e.*, a complex of cellulose nitrate and camphor. The final film, however, would probably be cellulose nitrate alone, since camphor is sufficiently soluble in water to be completely extracted from such a film in a very short time. It is probable that measurements of the thickness of such films would yield valuable results if they were correlated with the viscosity of the nitrocellulose, which is believed to be a function of the complexity of its molecular structure. The problem of deciding how the film is built up from the various sizes of particles believed to be present in these solutions is, however, much more difficult.

Experiments by Laird [37] throw some doubt on the validity of the calculations by which Barton and Hunt checked the thickness of the films. She measured the thickness of very thin films by an interferometer method, and assuming that the optical thickness is the true thickness, found that the density of the celluloid remained approximately constant at 1·41 down to a thickness of 400 $\mu\mu$ ($= 4 \times 10^{-5}$ cm.). Below this thickness, the density begins to increase. In the neighbourhood of 60 $\mu\mu$ (6×10^{-6} cm.) it is about 2 and at 30 $\mu\mu$ (3×10^{-6} cm.) it is about 2·5.

* Cf. p. 28.

Chromatic Emulsions.

In experimenting on the production of transparent emulsions, by emulsifying two immiscible liquids of equal refractive index, Holmes and Cameron [38] succeeded in obtaining some very striking chromatic emulsions using a solution of cellulose nitrate in amyl acetate as the emulsifying agent. Their directions for a lecture experiment as are follows : 4 volumes of glycerol and 4 volumes of a 2 to 4% solution of cellulose nitrate in amyl acetate are shaken together to form an emulsion. To this is added 5—10 volumes of benzene (toluene may be substituted), then more glycerol until the emulsion is somewhat viscous, and finally benzene again in small quantities until the colours appear. The order in which the pairs of colours appear with the addition of benzene is yellow and blue, pink and green, peacock-blue and pale yellow. If more benzene is added, the colours disappear and the emulsion becomes milky, but the addition of amyl acetate will bring them back in the reverse order. Chromatic emulsions have been known for many years, and can be produced, for example by emulsifying oil of turpentine and glycerol. Holmes and Cameron's emulsions, however, are more beautiful and permanent. If the emulsions are allowed to stand, a cream separates which shows the colours very clearly, and this can be separated from the lower layer. A quantity of this emulsion made by the writer nearly two years ago has retained its chromatic properties without change, except that the cream is now a semi-solid gel showing brilliant pink and green interference colours, altering with change of temperature.

The theory of chromatic emulsions is discussed by Holmes and Cameron (*loc. cit.*). They are due to the presence of two phases nearly equal in refractive index but differing considerably in optical dispersive power.

*Transport of Cellulose Ester Solutions on British Railways.**

Cellulose ester varnishes are classified by the British railways under the general heading of Inflammable Liquids, Class A, and the regulations controlling the traffic are printed in the " General Railway Classification of Goods " published by the Railway Clearing House. It is possible to find variations in the classification, but the policy of the railway companies, after having safeguarded the interests of passengers and of the owners of other merchandise in transit, is to meet the requests of traders as far as they can. The

* Mr. J. H. B. Jenkins, Chief Chemist of the London and North-Eastern Railway, has kindly read this section and checked the accuracy of the facts; for any comments or opinions the author alone is responsible.

variations, therefore, arise from the fact that different industries have asked for different facilities, which have sometimes been granted. The writer is glad to testify to the sympathetic hearing which manufacturers are given when they appear before a combined meeting of the chief chemists of the British railways.

The page references in the paragraphs which follow are to the current issue of the General Railways Classification of Goods, dated 1st April, 1924.

The varnishes appear in the classification under some unfamiliar names, derived sometimes from the trade names of the products made by the manufacturers who carried on the pioneer negotiations with the railway companies. Thus the cellulose nitrate varnishes appear as N.E. xylonite solutions (pp. 355 and 356), collodion (pp. 357 and 359), xylonite solution (p. 357), nitrocellulose solution (pp. 358 and 359), the initials N.E. signifying that the solution contains no ether. Solvents supplied for the dilution of the varnishes are described as N.E. xylonite thinnings, xylonite thinnings and collodion thinners. Aeroplane varnish or dope appears on p. 357, no distinction being made between nitrate and acetate dopes in view of the fact that the solvents in each constitute a similar fire danger.

The distinguishing feature of the inflammable liquids in Class A is that their flash point is below 73° F., the determination of the flash point being carried out in accordance with the directions of the first Schedule to the Petroleum Act of 1879. The instructions are reproduced on pp. 538–541.

The regulations may be summarised as follows : Cellulose esters under Class A were for a period subdivided (in effect) into those which contained ether and those which did not. The high vapour pressure of ether was regarded by the railway companies as justifying an extra precaution, which took the form of limiting the capacity of the containers, in which the solution might travel, to 10 gallons. Solutions not containing ether (N.E.) were allowed to travel in approved drums or barrels of anything up to 100 gallons capacity. This distinction has now been effaced by the entry on p. 359, allowing collodion also to travel in approved drums or barrels up to 100 gallons capacity. Since all solutions containing ether are usually grouped under the term collodion, the effect of this entry is in practice to put solutions which contain ether on the same basis as those which do not. Collodion thinners, however, p. 358, are still subject to the 10-gallon limit.

The specification for drums of 20 to 100 gallons capacity for this traffic is given on pages 527–528, and may be summarised thus :

They must be made of best soft iron or mild steel, with joints either riveted, soldered or autogenously welded; strengthened at each end by a strong iron or steel hoop shrunk on to the body, and provided with two rolling hoops welded or shrunk on. An alternative to the rolling hoops is the provision of two corrugations in the body protected by cover strips to specification. Barrels must have a bilge proportional to their length, the 33-inch barrel requiring a $2\frac{1}{4}$-inch bilge; they must also have end hoops, but need not have rolling hoops. The minimum thickness of the metal varies according to the size of the barrel according to the following table :—

Capacity.	Body.	Ends.
20 galls.	14 B.G.	16 B.G.
25—35 ,,	12 ,,	15 ,,
36—65 ,,	10 ,,	14 ,,
66—100 ,,	9 ,,	12 (barrels) 10 (drums)

Each drum or barrel must have a well-fitting screw bung, which must not project above the rolling hoops when screwed in. The boss must be autogenously welded or riveted and soldered to the body or end of the barrel. The drums must stand a hydraulic or air test of 10 lb. without leaking; this test to be repeated annually and whenever they show signs of damage. They must also be repainted or regalvanised as required to protect them from rust. The last two provisions are important—an air space of 5% must be allowed in filling and the bungs of empty barrels and drums must be securely screwed in before they are returned. The provision of the air space is to prevent bursting of full drums by rise of temperature, and the regulation about bunging the empties guards against the danger of accidental ignition of inflammable vapours remaining in the drum.

The specification for smaller drums, p. 524, of 1 to 15 gallons capacity is on similar lines, the differences being as follows : Strengthening hoops at each end are only required if the drum exceeds 12 gallons in capacity. The minimum thickness is 20 B.G. The screw bung and boss must be faced, and a washer provided, to ensure a good joint. (The bungs on these small drums are frequently wider than on the larger drums and barrels.) Drums for the export trade may have a bung or shive driven into a plain cylindrical neck, and covered with a soldered metal cap. In this instance the neck must be not more than $1\frac{1}{2}$ inches in diameter, and the top must be from $\frac{1}{8}$ inch to $\frac{1}{4}$ inch below the level of the chime.

The containers smaller than 1 gallon are used chiefly in the retail trade, and for a description of these reference must be made to the original classification. The chief safeguard consists in packing them in cases with sawdust.

Aeroplane dopes or varnish may travel in drums or taper-neck cans of 10 gallons maximum capacity (p. 529), and otherwise in wide-mouthed drums and taper-neck cans of 5-gallon and 10-gallon capacity (p. 533).

The thickness of metal is given in the following table :—

	5 gall.	10 gall.
Body of drums	22 B.G.	20 B.G.
Body, shoulder and neck of cans	,,	,,
Ends of drums	20 B.G.	,,
Bottoms of cans	,,	,,

The ends of drums and the bottoms of cans must be stamped out with a flange of $\frac{5}{8}$ inch to 1 inch, and placed on the body with the flange outward. These ends must either be swaged and welded, or welded and hooped as directed.

Two methods of closing the drums are allowed : (1) A cast-iron plug not exceeding $2\frac{1}{2}$ inches in diameter screwed with a leather washer into a flanged mild steel collar welded to the head of the drum at one side; (2) a well-fitting cork bung in a smooth neck of 4 inches diameter, with a metal capsule reeled over the wired edge of the neck.

Drums must be provided with handles welded, or riveted and welded, to the heads, but the handles and the screw bungs must not project beyond the end of the drums.

The taper-neck cans must have the shoulders autogenously welded to the cylindrical body, and the necks similarly attached to the shoulders. A 3-inch steel or brass ring must be welded or soldered respectively to the neck after galvanising. The ring is screwed to receive a screwed cast-iron plug with a leather washer. Two wrought-iron handles are welded on, one on each side of the shoulder.

A method is described for sealing the drums by means of a wire passing through the bung and the rim of the drum. Alternative arrangements are sanctioned.

The principal special regulations for the traffic are that each package must bear a conspicuous label " Highly Inflammable "; drums must be painted red at each end with the words " Highly Inflammable " in white letters; loading must be performed in day-

light, and the traffic must not be stored in any of the railway companies' enclosed sheds and warehouses. A special form of consignment note is necessary.

In regard to these regulations in general, it may be said that they are consistent with the principle mentioned in an earlier chapter of this book, that the danger of cellulose ester solutions is a function only of the inflammable solvents which they contain, and not of the solid contents. On the surface they appear somewhat onerous, but prospective users of such solutions should note that whatever burden they may place on the industry is borne almost entirely by the supplier and not by the user, except in so far as special regulations for the traffic must add something to the cost of the commodity. All that the regulations call on the consumer to do is to employ the special consignment note when returning empty containers to the supplier, and to replace the screw bungs securely.

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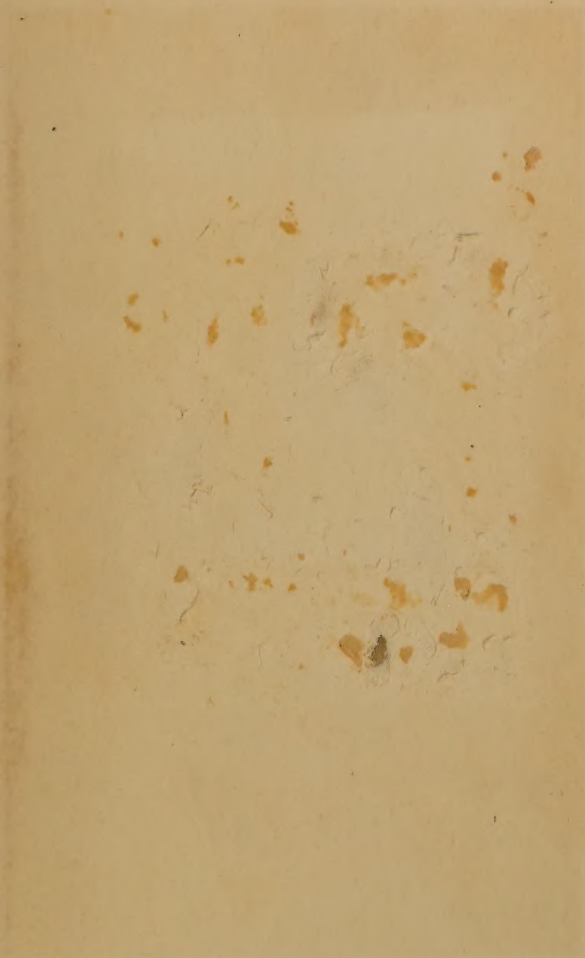

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